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ENGINEERING FINE PAPER BY UTILISING THE STRUCTURAL ELEMENTS OF THE RAW MATERIALS

Doctoral Thesis

Ramjee Subramanian

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Abstract

The objective of this thesis was to explore the possible ways of using the intrinsic properties of cellulosic pulp fibres and inorganic pigments, by combining these elements using non-standard procedures, as a means to engineer a new composite material – a novel uncoated woodfree paper with improved physical properties. Precipitated calcium carbonate (PCC) was used as the inorganic pigment in this study. To accomplish this objective, we conducted a preliminary study on web addition followed by detailed studies on in-situ precipitation in fibrillated pulp suspensions and blending of novel furnish materials. We evaluated the different technological approaches by analysing the production process and product quality.

In the first approach, chemical precipitation and spraying of filler dispersion onto a fibrous web, and mechanically pressing to assist penetration into the network, were compared against conventional filler dosage before web forming. The results showed that web addition approach results in higher tensile strength and lower light scattering of paper. Filler agglomeration and optical crowding, in chemical precipitation and web application respectively, resulted in significantly deteriorating the light scattering of the handsheets. The experimental conditions were not sufficient to obtain an even distribution of filler along the thickness direction of paper and the filler characteristics were not optimised in this study.

In the second technique, precipitation onto fibrillated pulp suspensions was investigated by varying the pulp substrate, PCC crystal structure, and pre-refining a mixture of pulp and milk of lime. According to the research findings, PCCs formed by precipitation of calcium carbonate onto cellulosic fibrils and fibres do not necessarily have the same characteristics as reference PCCs formed by carbonizing milk of lime. Precipitation of calcium carbonate onto fibrillated fibres and microfines increases the retention of filler but impairs the dewatering of handsheets during pressing. Higher amount of fibrillated cellulosic substrates in combination with appropriate filler morphology, scalenohedral or rhombohedral, contribute to increased bond strength and light scattering of traditional fine paper. Pre-refining a mixture of pulp and calcium hydroxide results in grinding of lime, and hence, the composites have a greater surface area than the reference filler. Composite filled handsheets, from this study, exhibited high light scattering.

In the third method, the microfines-filler composite was envisioned as the backbone structure for a new composite material – uncoated fine paper. In the new composite paper, strength properties arise from the microfibrillated cellulose, bulk and pores originate from the filler surrounded by fibrils, whereas tear strength is imparted by a minimal proportion of pulp fibres in the composite. Compared to conventional fibre based fine paper, even at high filler loading the new composite material showed higher bending stiffness, tensile and tear indices, internal bond strength, light scattering and brightness properties. The new concept of fines-pigment-based furnish enables us to load pigments in uncoated wood free paper up to 50%-60%. However, dewatering time is considerably longer. This method needs to be optimised, with further research on dewatering, and printability, before scaling it to an industrial process.

This study shows the potential of different approaches, novel furnish components and addition of pigment onto a formed web, in the creation of new composite fine paper. Novel composite structure for fine paper can be achieved by employing the smallest component of pulp fibres, cellulosic microfines, in combination with pigments. The characteristics of microfines and crystal structure of pigments are important control variables in the formation and properties of the new composite paper. On the other hand, cellulosic microfines are highly swollen and retard dewatering. Therefore, further optimisation of process methodology and product quality can be expected to lead to some useful advances in commercialisation of this technology.

Keywords engineer, composite, uncoated woodfree paper, filler, precipitated calcium carbonate, microfines, webaddition

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PREFACE

This study was carried out at the Department of Forest Products Technology, Helsinki University of Technology (HUT). The thesis has certainly been the most challenging work I have done so far in my life, a learning process beyond comparison in professional as well as personal terms.

First and foremost, I wish to express my warmest thanks to Prof. Hannu Paulapuro for his encouragement, his support in times of need and his guidance throughout the doctoral thesis work. I would also like to express my gratitude to my co-authors, Thad C. Maloney, Henrik Fordsmand, Eero Hiltunen, Taeguen Kang and Jouni Paltakari for their inspiring discussions, invaluable comments and manuscript reviews. Thanks are also due to all members of the laboratory for providing an excellent working atmosphere.

My sincerest thanks go to my family members for their unwavering support and love. The continued affection of all my friends is also gratefully acknowledged. Finally, without the unconditional love and personal commitment of my wife, Umamaheswari Balasubramanian, and smiles of the children, Ashwin and Sruthilaya, I would not have been able to finish this work.

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LIST OF SYMBOLS AND ABBREVIATIONS

$(NH_4)_2CO_3$	Ammonium carbonate
BET	Brunauer-Emmett-Teller
$CaCl_2$	Calcium chloride
CD	Cross-machine direction
C-PAM	Cationic polyacryl amide
DDJ	Dynamic drainage jar
ECF	Elemental chlorine-free
FIB-SEM	Focussed ion beam-Scanning electron microscope
GCC	Ground calcium carbonate
HWI	Mixed hardwood pulp from India
ISO	International organisation for standardization
LSC	Light scattering co-efficient
MBF	Moving Belt Former
MD	Machine direction
MPS	Median particle size
MTS	Material testing system
Na_2CO_3	Sodium carbonate
PCC	Precipitated calcium carbonate
c-PCC	Colloidal precipitated calcium carbonate
r-PCC	Rhombohedral precipitated calcium carbonate
s-PCC	Scalenohedral precipitated calcium carbonate
SEM	Scanning electron microscope
WFU	Wood-free uncoated fine paper

INTRODUCTION

The oldest inventions for the needs of human communication include bone, stone, clay tablets, various metals, papyrus and paper. With the advent of the industrial revolution, paper became a tool of mass communication, ultimately leading to the emergence of mechanized papermaking technology. Historically, the role of paper has changed with different levels of communication during the development of human civilisation.

In today's global society, characterised by information glut and modern electronic communication systems, paper and paper-like products have assumed a supportive and complementary role. This role is effectively fulfilled by printing and writing paper commodity grades in collecting, distributing and storing information.

The printing and writing paper industry is a global industry based on a renewable raw material, cellulosic pulp. World demand for graphic paper is currently 78 million tons a year and it is expected to grow at an average rate of 1-4% per annum until 2010. Printing and writing papers are divided into mechanical pulp-dominated and chemical pulp-dominated grades based on the nature of the main raw material, pulp (Haarla 2000). Offset papers and light-weight papers are classified as uncoated fine papers, also called wood-free uncoated fine papers (WFU).

In the printing paper industry, the driving forces affecting profitability are the variable costs, operating rates and efficiency, sales prices and currency fluctuations (Haarla 2003, Diesen 1998). Variable costs, which includes the cost of materials, is a crucial control variable in papermaking. Profitability is also strongly affected by sales prices. Printing and writing paper is one of the most technically advanced grades of paper, meeting demanding and comprehensive manufacturing specifications and satisfying the requirements for end-use properties.

Since the advent of papermaking technology, inorganic pigments have been an important tool in decreasing the material costs of the papermaking process, and thus, enhancing the profitability of the paper industry. Fillers are cheap white mineral pigments – typically priced at 20% of pulp market prices – which are used to improve dewatering and paper properties. Hence, the study of inorganic and organic pigments has been of great interest to the papermaker.

Today, there is a wide variety of fillers suited for acid, neutral and alkaline papermaking conditions. The amount of pigment added to paper normally varies from 5% to 35%, and considerable knowledge has been accumulated about the way in which pigments interact with fibres and other components in the papermaking system. There is a need to increase the mineral fraction in paper and to decrease paper grammage, while keeping critical paper properties at an acceptable level.

Increasing amounts of filler impair the strength and stiffness of paper, limiting the proportion of pigment in a conventional fine paper to 20-25%. Recently, various methods have been examined to find a way to increase the amount of calcium carbonate in paper without sacrificing paper quality. Thus, it is of great importance to

the papermaker to innovate and develop new raw materials, raw material combinations and process technology in order to create value for the papermaking industry. Hopefully, the innovations will lead to a reduction in raw material costs, lower grammage, improved sheet quality and development of more sustainable process for production. Thus, the overall objective of this thesis was to construct a novel and improved fine paper by modifying or blending the structural elements of cellulosic pulp fibres and pigments, and to study the forming process and product properties.

The main objective was divided into the following sub-objectives:

1. Identifying new methods of pigment addition and fine paper forming.
2. Finding out how to increase the fraction of filler in WFU paper with micro-fibrillar cellulose and pigment combinations.
3. Developing a method of precipitating calcium carbonate (PCC) onto refined cellulosic pulp fibres and microfines. (The blend of calcium carbonate on the pulp fibril is termed 'composite filler').
4. Clarifying the impact of PCC-microfines composites in the forming and wet pressing of fine paper.
5. Determining the influence of new methods of forming and composite PCCs on the strength, optical, and print rub-fastness properties of WFU paper.

Hypotheses

The experimental work needed to achieve the above-mentioned objectives was based on the following hypotheses:

1. It is proposed that the properties of paper are determined not only by the attributes of the furnish component fractions that compose it, but also by the manner in which these components are assembled. If this general hypothesis is true, then it should be possible to achieve different, and possibly advantageous paper properties by using forming methods other than those used in present industrial practice.

2. More specifically, it is proposed that a new gamut of properties for a fine paper sheet can be achieved, even when using essentially the same gross composition, by introducing the filler after the structure of the paper has been formed. A further motivation for investigating this hypothesis is to simplify the overall papermaking process. In the traditional fine paper production, addition of filler to the base furnish results in complex wet end chemistry, lower filler retention during forming and reduced paper strength. On the other hand, introducing filler into a wet sheet of paper, after it has been formed, should contribute towards improving the papermaking process and paper properties possibly due to the following factors:

    a. Increased control of forming process chemistry and white water system closure.

    b. The interfibre bonding might not be affected by the presence of filler as they should deposit only outside the area of fibre crossing.

    c. Individual filler particle deposition might be more effective in scattering light.

3. It has been enunciated that paper is a bonded network of cellulosic fibres whose crucial physical properties, strength and light scattering, can be varied by changing the fibre length, strength, coarseness, perimeter, specific bond strength and relative bonded area. Further, it has been shown that the light scattering efficiency in filled sheets is directly related to the extent of surface area associated with optically effective pores, i.e., greater than 0.1µm.

It is proposed that manipulation of bond properties and number of optically effective pores, by means of a co-precipitation method, will make it possible to increase filler amounts, improve paper properties and reduce basis weights of fine paper. The product performance of PCC precipitated on top of pulp fibrils can be optimised by modifying the raw material components, methods of production and crystal habits of the precipitate.

4. It has been shown that the weakening of paper by filler can be effectively compensated by augmenting the amount of microfines. Therefore, it is proposed that a microfines-filler base furnish should be more effective than a fibre-filler furnish in allowing an increased amount of filler pigments in paper. Thus, we envisioned a microfines-filler composite as the backbone structure for a new composite material – uncoated fine paper. In the new composite paper, the strength properties arise from the microfines, bulk and pores emerge from the filler surrounded by the microfines, while tear strength is provided by the minimal fibre fraction in the composite.

The thesis consists of six publications. Table I shows the correlation of the publications with the above-mentioned sub-objectives of the thesis, including references to the chapters in the thesis summary.

Table I Correlation of publications with chapters in the summary and thesis sub-objectives within the published papers, denoted by roman numerals.

Publications		**Objectives**	**Chapters in thesis compendium**
I	Wet web addition of calcium carbonate filler	1,5	2
II	Calcium carbonate composite fillers	1,2,3,5	3
III	Calcium carbonate – cellulose fibre composites; The role of pulp refining	1,2,3,4,5	3
IV	Effects of PCC-bagasse pulp composites on printing and writing paper properties	1,2,3,4,5	3
V	Precipitated calcium carbonate (PCC) – cellulose composite fillers; Effect of PCC particle structure on the production and properties of uncoated fine paper	1,2,3,4,5	3
VI	A new composite fine paper with high filler loading and functional cellulosic microfines	1,2,3,4,5	4

Publications

I Subramanian R, Hiltunen, E. and Paulapuro, H. (2005). “Web addition of calcium carbonate filler”, *Inpaper International*, 7(3), 14-23.

II Subramanian R., Maloney T. and Paulapuro, H. (2005). “Calcium carbonate composite fillers”, *Tappi J.*, 4(7), 23-27.

III Subramanian, R., Maloney, T., Kang, T. and Paulapuro, H.: "Calcium carbonate-cellulose fibre composites – The role of pulp refining", *Paper technology*, 47(8), 27-31.

IV Subramanian, R. and Paulapuro, H. (2006). "Effect of PCC-bagasse pulp composites on printing and writing paper properties", Proceedings of *New technologies in non-wood fibre pulping and papermaking*, Zhan Huaiyu, Chen Fangang and Fu Shiyu (eds.), South China University Press, 270-276.

V Subramanian, R., Fordsmand, H. and Paulapuro, H. (2007). "Precipitated calcium carbonate (PCC) – cellulose composite fillers: Effect of PCC particle structure on the production and properties of uncoated fine paper", *BioResources* 2(1), 91-105.

VI Subramanian R., Fordsmand, H., Paltakari, J. and Paulapuro, H. (2008). "A new composite fine paper with high filler loading and functional cellulosic microfines", Manuscript accepted for publication in Journal of Pulp and Paper Science.

Author's Contributions

In the above publications I-VI, the author completed the following:

All experiments, the main part of the analyses and the first version of the manuscripts.

CHAPTER 1

Fine papers are referred to as “wood-free” papers produced from fully bleached hardwood and softwood chemical pulps with the addition of fillers. Recently, some office paper grades have been produced with a 10% share of mechanical or chemi-mechanical pulps. For office paper grades, a typical furnish consists of 60% - 100% hardwood kraft pulp, 0-40% softwood kraft pulp, 10-30% fillers, minor amounts of optical brighteners, starch, hydrophobic size, retention aids and other chemicals and additives.

During forming, fibres and particles in the papermaking furnish can be retained by two basic mechanisms: mechanical or colloidal. Traditionally, pigment fillers and fines can be incorporated in a fine paper as individual particles or aggregates, by filtration-based, deposition-based or mechanical entrapment mechanisms, using five related methods /van de Ven 2005/:

- by deposition on fibres suspended in the papermaking furnish, in the approach flow, headbox, slice or in the drainage section prior to reaching the dry line /van de Ven 1989, van de Ven et al. 2004, Lindström 1989/

- by deposition on fibres which that are incorporated in the forming sheet (during drainage) /van de Ven 2001, Alince, et al. 2002_b/

- by homo-flocculation of fines or fillers, and subsequent entrapment of aggregates in the sheet /Holm and Manner 2001, Porusbska, et al. 2002/

- by hetero-flocculation of fines and fillers, and subsequent entrapment of aggregates in the forming sheet /Gavelin 1988/

- by deposition of fillers on fines which are subsequently captured in the forming sheet /Silenius 2002/

The quality requirements for the functional behaviour of different fine paper grades may be very different in terms of formation, strength and optical properties. The factors responsible in practice for the structure of paper are the papermaking furnish components, the amount and characteristics of the retained components and the treatments given to the formed web. In practice, this translates into varying demands for raw material composition, layering of paper and surface treatments.

Basically, papermaking is the assembly of fibres into a sheet by a process which does not in any way control the deposition of individual fibres. It is generally desired that the sheet be uniform throughout, or as nearly as possible. On the other hand, non-uniformity is an inherent property of stochastically formed fibre networks like paper.

A simplified structure of printing and writing paper is depicted in Fig. 1. The structure of paper has been defined to be the geometric arrangement of fibres and interfibre spaces or pores. Accurate description of the structure of paper is complicated due to the random, intertwined, porous geometry and the presence of constituents with different morphology, such as fibres of different size, fines and fillers. However, network models have been proposed considering paper as a simplified micro-structure, idealised fibres and bonds as basic structural elements and relating the mechanical properties of the network to the characteristics of these elements. For example, six closed-form networking models have been enunciated to relate the tensile strength of paper, a critical property to withstand a certain amount of stress and strain in printing and converting operations, to the structure of the fibre network /Jayaraman and Kortschot 1998/.

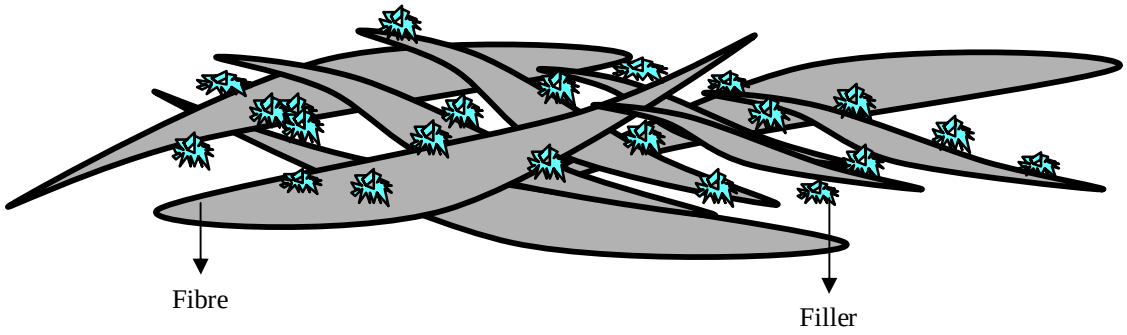

Figure 1 Network structure model of printing and writing paper.

Based on the structure of paper as two-dimensional thin sheet layers, as articulated by Kallmes and co-workers, Scallan and Borch /Scallan and Borch 1972/ describe the reflectance of a sheet of paper in terms of a layer model. The reflectance of paper is considered as the result of a large number of simple reflection and absorption processes within this model. Instead of using the specific absorption and specific light scattering coefficients (k and s) of the “Kulbelka-Munk” treatment, the light scattering process has been described in terms of new constants, i.e., reflectivity, transmittivity and number of layers (r, f and n).

Modelling of the paper structure based on pore height has been proposed and studied by Niskanen and Rajatora /Niskanen and Rajatora 2002/. The model relates pore height, determined from light microscopic image cross-sections, to the porosity and relative bonded area of paper. Considering paper as a continuous solid phase containing air voids that are scattering elements, Alince and co-workers related light scattering of paper to the surface area of optically effective pores, i.e, pores greater than 0.1µm /Alince, et al. 2002_a/.

In an assembly of stochastically oriented fibres, scattering of light takes place at the interface of the fibre surface and air. Therefore, the amount of scattered light per unit mass will depend on the extent of such an interface /Retulainen 1997/.

Optical properties = f (unbonded area) = f (total area – bonded area) (1)

In view of the above relationship, the optical properties of paper can be improved by augmenting the unbonded area. The unbonded area can be expanded by either increasing the total surface area or decreasing the bonded area.

According to Retulainen /Retulainen 1996/, a reduction in the grammage of printing paper can be achieved by two methods:

1. by forming stronger bonds by enhancing the specific bond strength, obtained by dividing the strength of the interfibre bond by the area of the bond. A feature of practical importance is that if the fibre properties can be varied so that certain tensile strength can be achieved at lower relative bonded area (RBA) then the optically active surface area of the sheet will be higher.

2. by simultaneously increasing both the total area and the bonded area of a dried paper. This can be done, for example, by reducing the average coarseness of fibres or adding fines to the sheet. In his work, the author deals with mechanical pulp dominating grades in the absence of filler.

Bending stiffness is an important property for printing and writing paper. Two fundamental components of bending stiffness are the elastic modulus and thickness of paper. In a homogeneous structure, bending stiffness is expressed as (Kajanto 2000):

$$s = E * t^3 / 12 \qquad (2)$$

where E is called the elastic modulus or Young's modulus (N/m^2 or Pa) and t is the thickness of the material. Based on this formula, the bending stiffness of paper is expected to be directly proportional to the elastic modulus, and to the third power of the thickness of the sheet.

1.1 Quality requirements for printing and writing papers

The quality requirements for various uncoated fine paper grades are quite different in terms of formation, strength and optical properties. To meet these demands, the raw material composition has to be varied. The requirements of layered structures and surface treatments are also grade-dependent. In addition, minimum two-sidedness of material distributions and surface quality is a desired quality, common to most printing and writing papers.

The critical properties of printing and writing office papers are /Charles 1981, Dewitz 2004, Häggblom-Ahnger 1998, Paulapuro 1992/:

1. Caliper
   Caliper should be controlled with very low variations, and varies depending on the type of printing press or copier. Control of pre-calendered caliper and grammage will improve control of other properties, such as the final smoothness and stiffness.

2. Strength
   Strength is the property of paper that allows it to withstand the stresses placed on it during any imaging and converting processes. Higher strength contributes to increased runnability of the web-fed printing press.

3. Good appearance and formation
   These properties are increasingly important due to greater demand for multicolour copying and printing. With more uniform formation, higher surface smoothness can be achieved in calendering without as much decrease in bulk and compressibility. Good formation uniformity required for uniform absorption properties and strength properties of paper.

4. Optical properties are crucial in high-quality office papers
   Printability properties can be divided into two parts: optical and functional. Optical properties include opacity, shade, brightness and gloss, which are, in addition to uniform formation, the basic elements of good visual appearance and print quality.

   Print density, a relative measure of the average darkness of print, is defined as follows /Karttunen, 1973/:

$$D = \text{density of solid print} = \log\left(\frac{\text{Luminous reflectance of paper}}{\text{Luminous reflectance of print}}\right)$$

   Thus, the print density depends on the diffuse and specular reflectance of the unprinted paper. Hence, higher light scattering and opacity are required for high quality printing and writing paper.

5. Good surface smoothness, high bulk and stiffness
   Colour printing and copying requires paper with high smoothness. Smoothness plays an important role for digital print image quality because of the irregular toner particle sizes used in printing systems. The absence of surface irregularities in paper allows the toner particles to adhere to the surface more uniformly, which creates a better image. Final smoothness in paper is obtained by light calendering, where bulk and stiffness are simultaneously reduced.

   Cross-directional stiffness is more critical, as it tends to be lower due to fibre orientation in machine direction. Most A4-size copy papers are cut along the grain and are fed into the copy machine in cross direction. Low stiffness can lead to jams in cut sheets and misfolds in continuous-form paper.

6. Low curling during moisture and temperature changes
   In electrophotographic printing, common curl-related problems are in post-copier curl, which is induced in the sheet by the heating action of the fuser. The heating of the sheet is not uniform relative to the paper's thickness

dimension and lowers the moisture content in a non-uniform manner, creating stresses of different amounts on each side of the sheet, with the consequence that the paper curls preferentially towards one side. In many cases, the curl is towards the side onto which the image has been copied. High curl frequently lead to jams, feeding failure and poor roll stripping, a tendency for the print substrate to remain tacked to the fuser roll after passing through the nip between the fuser roll and the pressure roll and does not follow the normal printed substrate path, in printers.

Irrespective of the directions of post-copier curl, the degree of curl and dimensional changes should be minimal to prevent delivery and collating problems. Moisture content is of prime importance in keeping curl toward the first pass printed side. Research literature published by IBM suggests that moisture should be kept within the range of 3.4% -5.5% /Borch and Svendsen 1984/. A paper with a moisture content of 4.5% usually performs well in printing and copying machines, provided it meets the requirements for curl and resistivity.

7. Low cockling tendency
   Small-scale differences in material structure, grammage instability (residual variation), poor formation and fibre orientation lead to cockling of paper as a result of uneven drying of paper. Sheet flatness is important in preventing print deletions (sometimes called voids).

   Laser printing and continuous stationery require accurate MD orientation to avoid problems with leaning paper piles.

8. Friction and surface strength
   Good printing and copying requires paper with high friction and surface strength. Lower friction and surface strength leads to friction feeding failure or slippages in continuous-form printers. Bonding sufficient to prevent contamination is usually obtained by a good coverage of surface size. Maintaining filler content at a reasonable level is also desirable. Felt side contaminations, due to low surface strength, results in misfeeds or multi-feeds in copy machines.

9. Electrical resistivity
   The electrical properties of copy paper have an important role in quality image production. Paper with a high resistance to electrical charge will hamper the toner transfer process and will result in poor image quality. If the paper enters the process with low charge properties, toner adhesion problems may result. Paper entering the printer with high charge, or with a characteristic to hold high charge, may cause a build-up of static electricity. Moisture control in the paper sheet is critical for managing surface resistivity. Ensuring uniform surface resistivity requires the moisture content of the paper to be spatially uniform

10. No or minimal linting
    In printing and copying, sometimes a weak surface of paper will be abraded by a friction-type feeder causing feed roller contamination and even delamination

of the sheet. In offset printing, printing nips require that the paper surface endure the forces that arise as the ink films split in transfer to paper, especially in the presence of dampening water. Hence, surface strength is a crucial requirement for printing papers.

1.2 Raw materials affecting the properties of printing and writing paper

1.2.1 Cellulosic fibres

Natural cellulosic fibres are the most important raw materials of paper and paperboard, and of many hygiene products. Table II demonstrates the major structural scales in papermaking, and the relationship between fibre structure and paper properties at each of these levels /Kortschot 1997/.

At the molecular level, cellulose is the main load-bearing component in fibres. It is a linear polymer composed of glucose units joined together by β- 1,4 glycosidic bonds /Hinterstoisser 2001/. Cellulose has a strong tendency for intra- and intermolecular hydrogen bonding, which leads to the formation of fibrils with excellent mechanical properties (Rånby 1957). During their biosynthesis, microfibrils having dimensions of 3.5*3.2 nm /Paavilainen 2002/, aggregate into larger units in the cellulosic fibre. Cellulosic fibrils are the load-carrying elements in fibres. Gurnagul and Page /Gurnagul and Page 1989/ have suggested that fibrils are the main components influencing the viscous response of fibres. Fibre strength and stiffness significantly depend upon the micro-fibrillar angle in S2 and S1 layers, if intact /Page and El-Hosseiny 1983/. In addition to cellulosic fibrils, bleached chemical pulps contain hemicellulose, very smalls amount of kraft lignin and metals /Wågberg and Annergren 1997/.

The cell walls of dry fibres are quite non-porous. In wet state cellulosic fibres, whether native or processed, have a porous structure /Stone and Scallan 1965/. The porosity has a large effect on fibre swelling, which is a property relevant to the fibres' ability to build strong networks. In refining, porosity is introduced to the fibres by mechanical action and rupturing of microfibrils. The entry of water into the fibres causes debonding and separation of the solid elements /Scallan 1977/. Wang /Wang 2006/ explains that for never-dried fibres, refining mainly expands the large pores in the cell wall, whereas it has only a slight effect on the small pores. For dried fibres, refining not only expands the large pores but also reopens the small pores to a certain extent. On the other hand, Wang postulates that refining does not completely reverse hornification. Charges on fibres /Scallan 1983, Lindström 1982/ significantly change the swelling of pulp fibres.

Morphological properties of fibres, fibre length, fibre width and cell wall thickness vary a lot depending on the type of raw material, wood or non-wood species, within annual growth rings of wood, growing conditions and pulping process conditions. In a specific pulp the morphological properties differ significantly between fibres. Jang and Seth /Jang and Seth 2004/ stress that the mass-weighted mean fibre length is the

Table II The hierarchical structure of paper /Kortschot 1997/**.**

Scale	**Structural component** o various types at the level	**Structural parameters** o characterizing spatial distribution of mass only	**Properties dependent on structure at this scale**
0.1 nm – 10 nm	o Molecular structure and packing o Cellulose o Hemicellulose o Lignin o Other components	o Molecular weight o Stereoregularity Chemical composition – (type and number of bonds, functional groups, etc.,) o Crystal structure o Free volume o Aspect ratio of elementary fibrils (crystallites) o Fibrillar defects	o Hydrogen bonding potential o Tensile modulus and strength of fibrils o Tg of lignin o Influence of moisture on Tg, stiffness o Viscosity o x-ray diffraction properties
10 nm – 1 µm	o Internal structure of the fibre o Softwood tracheids o Hardwood fibres o Hardwood vessels o Ray cells o Compression wood o Tension wood	o Volume fraction and position of the various components of the cell e.g. for softwood tracheid: P, S1, S2, S3, W o Wall thickness o Lumen diameter Pit location and density Fibril angle in each layer o Cracks o Internal fibrillation, porosity o External fibrillation	o Stiffness and strength of the fibre o Anisotropy o Distribution of weak spots along fibre o Bond strength o Moment of inertia of cell walls o Light scattering o Fibre saturation point o Swelling potential
1µm–10mm	o Fibre morphology Different types of fibres: softwood fibres, tracheids, hardwood fibres, hardwood vessels, ray cells, fines	o Length, width, thickness o Moment of inertia o Curl, kinks o Microcompressions o Specific surface area o Fines content and type (“quality”)	o Fibre strength, distribution of strength o Fibre modulus, stress/strain curve, wet web strength o Shear and torsional properties o Fibre flexibility o Collapsibility o Hygrothermal properties (transverse and axial)
1µm-10mm	o Paper microstructure	o RBA o Fibre orientation distribution o Density o Fines distribution (location) o Porosity, pore size distribution o Surface texture o Shive content o z-direction distributions (two sidedness)	o Local sheet properties – strength modulus, stress/strain curve o Tear strength and fracture toughness o Peel strength/ delamination resistance o Viscoeleastic properties o Printability o Linting o Opacity o Surface feel o Absorbency
1mm - 10 cm	o Paper mesostructure	o Distribution of mass Distribution of regions with net differences in microstructure such as average local fibre orientation, local density or local relative bonded area	o Optical formation o Printability o Tensile strength of the sheet
5mm - 30m	o Paper macrostructure	o Roll defects Roll structure (density profiles, etc.,) MD and CD variations in sheet and roll structure o Multilayered structure	o Converting performance o End-use performance

most relevant fibre length measurement over arithmetic mean or length weighted mean fibre lengths. Fibre structural dimensions may vary for different wood and non-wood species, and the softwood species exhibit the greatest size, as enumerated by Peel /Peel 1999/.

Fibre deformations, such as curl, kinks, dislocations and microcompressions affect the stress-strain behaviour of fibres /Page and Seth 1980/. Fibre damage leads to a reduction in strength of dry or wet fibres and fibre networks /Joutsimo, et al. 2005/.

1.2.2 Pulp fines

Fines in chemical pulps can be broadly classified into two types: primary and secondary. Primary fines are small particles originally present in the wood, such as, shortened fibres, vessel elements and ray and parenchyma cells. Secondary fines are generated during mechanical treatment of pulp fibres.

This section focuses on the secondary fines produced by mechanical treatment of chemical pulp fibres. The fines content of a material with a certain particle size distribution is defined by its weight fraction that passes through an opening of a certain size. The size of the opening is arbitrary. For papermaking materials, generally particles that pass through a 75 µm diameter round hole or a 200-mesh screen of a fibre length classifier are regarded as fines /Retulainen 1997/. Particles of this fraction are appreciably smaller than those of the fibre fractions, generally being smaller than 200 µm. The smallest particles are of fibrillar nature and have widths in the range of 0.02 µm-0.5 µm.

Retulainen and co-workers /Retulainen, et al. 2002/ have characterised and analysed the significance of fines. According to their findings, the BET specific surface area of freeze dried bleached softwood kraft fines is in the range of 15-25 m^2/g. Fines quality was described on the basis of the size and shape of particles. Size determination contained equivalent and maximum diameter while raggedness and oblongness were used to characterise the shape. The fines are more swollen and carry nearly twice the amount of water per unit dry mass compared with fibres, Fig. 2 /Laivins and Scallan 1996/. Fines can drastically decrease pulp freeness and sheet porosity /Seth 2003/. Reduced porosity retards moisture escape and slows the drying rate. Fines have a great effect on paper web shrinkage, increasing the shrinkage degree and decreasing the web dryness at which the shrinkage begins compared to a fibrous web /Przybysz and Czechowski 1985/.

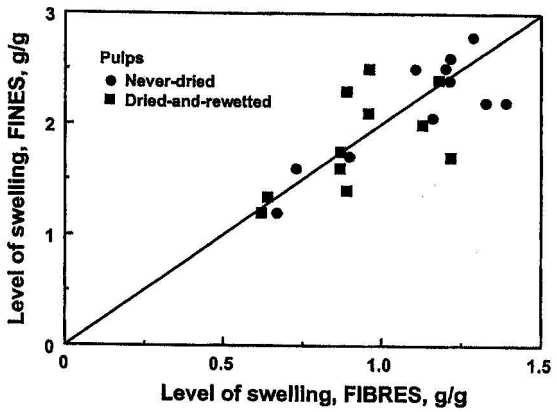

Figure 2 The level of swelling of the fines fraction is almost double that of the fibre fractions. The pulps included both commercial and laboratory-made, chemical and mechanical pulps from hardwoods and softwoods /after Laivins and Scallan, 1996/.

Several researchers have examined the effects of chemical pulp fines on paper /Retulainen 1997, Seth 2003, Retulainen, et al. 2002, Sirviö and Nurminen 2004/. In these studies, fines were found to increase density, augment sheet consolidation and fibre-fibre bond strength, and improve stress distribution due to greater sheet shrinkage. In filler-containing sheets /Xu and Pelton 2005_a/, fines act as a glue and increases the contact area in fibre-to-fibre and filler-to-fibre adhesion. Giertz /Giertz

1980/ proposes that fines covered with swollen hemicellulose increase the amount of bound water and form a strong wet adhesion system. Fines behave as a swollen gel with high internal capillary porosity /Marton 1980/. They form the bonding layer with external fibrils /Nanko and Oshawa 1989/. The bonding layer is charactereised by skirts, longitudinal wrinkles and covering layers. The bonding layer contributes substantially to the increase of the contact area by filling gaps caused by the surface irregularity of bonded fibres. Fines are deposited in the fibre network near the bonded areas and corners in such a way that the effective length of free segments shortens, making them easier to "activate"/ Vainio 2007/. Therefore, fines improved most sheet strength properties of the pulp. Improved wet web strength and wet web stretch can be obtained with increasing amounts of different fractions of fines, as illustrated by Paasonen /Paasonen 1968/. On the other hand, in spite of their large specific surface area, chemical pulp fines do not contribute much to the light scattering of paper (Fig. 3). This is because chemical pulp fines are flexible and readily bond to fibres during drying, thereby losing their free surface that scatters light /Retulainen, et al. 2002/.

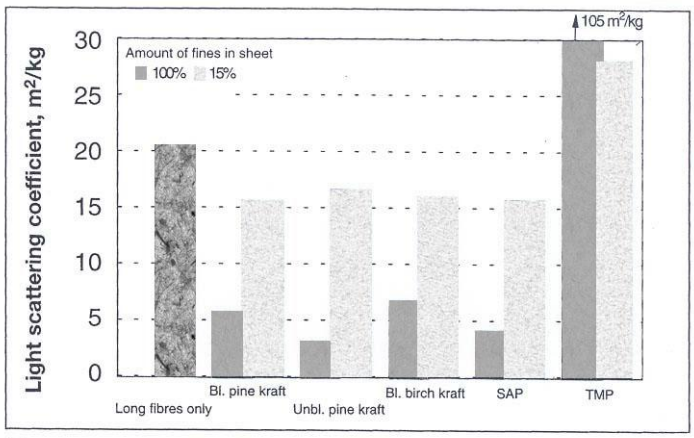

Fig. 3 **Effect of fines addition on the light scattering coefficient of kraft fibre handsheets.**

Figure 3 Effect of fines addition on the light scattering coefficient of kraft fibre handsheets. The pulps included bleached and unbleached softwood, semi-alkaline spruce sulphite pulp (SAP) and spruce thermomechanical pulp (TMP) /Retulainen, et al. 2002/.

1.2.3 Mineral pigments

Pigments have been an integral component of papermaking, with or without the papermaker's knowledge, since the beginning of papermaking in Europe /Dabrowski 2003/. Filler pigments are incorporated into printing and writing papers to decrease manufacturing costs, improve brightness and light scattering properties, and to improve the quality of the printed image.

Pigment addition results in a loss of tensile strength due to the reduced proportion of load-bearing fibres and interference with the bonding between fibres /Krogerus 2000/. Some fillers types are more detrimental to paper strength than others. For example, when compared at a constant total area of filler per mass of paper, burst strength declined in the order clay>talc>GCC /Miller and Paliwal 1985/. GCC and PCC show similar effects, while prismatic PCC is less harmful to strength than scalenohedral PCC /Middleton and Scallan 1989, Bown 1998, , Xu, et al. 2004/. For a given type of filler, the smallest fillers have the most detrimental effect on paper strength /Li, et al. 2002/.

In the traditional approach, the light scattering coefficient of paper is considered to be due to multiple reflections and refractions at the air-fibre interface, and a linear relationship between the specific light scattering coefficient (LSC) and specific surface area is observed /Scallan and Borch 1974/. Another approach /Lepoutre, et al. 1989/ considers highly filled paper as a microporous system and thus, a relationship is derived between the wavelength dependence of the light scattering coefficient and the pore size distribution, characterised using the wavelength dependence of the light scattering coefficient of paper. The effect of formation uniformity on opacity and light scattering has been studied by Jordan /Jordan 1985/.

The apparent light scattering coefficient of a given pigment in filled papers depends on the state of pigment dispersion and the beating level of fibres. Since pigment addition leads to a loss of tensile strength, which is most pronounced with dispersed and smaller-particle-size pigments, a plot of optical properties versus tensile strength provides a means for evaluating pigment effectiveness and for comparing different pigments /Alince 1989/. A mechanistic model for the interaction of filler and fibre, providing a quantitative expression that relates light scattering to the effect of filler on the fibre as represented by the change in sheet strength, has been derived by Bown /Bown 1985/. The model assumes that the refractive index of the filler is sufficiently close to that of cellulosic pulp, and minimal light scattering takes place at the fiber-mineral interfaces.

Thus, for a filled sheet, the light scattering coefficient is assumed to have three components:

1. Light scattering from the non-bonded fibre area
2. Light scattering from fibre fines and fibrillation prevented from collapsing by the filler
3. Light scattering from the filler

With the conversion to alkaline papermaking, the use of precipitated calcium carbonate as a paper filler is increasing because of its ability to enhance the properties of paper, such as brightness, opacity, bulking ability, permanence, air permeability, softness and lower abrasiveness. The physical properties of calcium carbonate pigments that are crucial in determining critical paper properties are particle size and shape, particle size distribution, particle void volume and specific surface area /Bown 1997, Raymond, et al. 2003, Phipps 2001/.

CHAPTER 2

2.1 Introducing filler into a wet web of paper

Blending of pigments into a stock suspension adds to the challenges of the papermaker. These challenges include controlling the retention of filler, grade changes and system stability. Pigments also can result in the formation of deposits in the wet end of the paper machine. These problems can be resolved by adding the filler to the wet web of paper after forming.

It was hypothesized that adding filler after the inter-fibre bonding areas have been established would minimise debonding, and hence, paper strength can be maintained at a relatively high level compared to conventional paper. Moreover, adding the filler to the web gives the possibility to control the z-directional filler distribution in paper. Accordingly, the objective of the preliminary work described in this chapter was to find a means to apply the calcium carbonate filler particles into the wet-web of fine paper furnish after forming, and to study the properties of the paper formed by this process. We aimed to obtain an even distribution of filler in the thickness direction of paper.

In 1947, Muggleton /Muggleton 1947/, patented a method for adding filler to the web. The patent involves the application of filler through a chute to the dandy roll of a fourdrinier former. Studies by Alince, et al. /Alince 2002_b/ showed encouraging developments in web addition of filler. Their findings had shown that the electrostatic attraction between oppositely charged fibres and clay particles can result in fast and full coverage of the fibres when a clay suspension is passed through a wet fibre web. With a suitable amount of filler and suitable electrostatic interactions and pH conditions, high filler retention, uniform distribution and full coverage of all the fibres with filler can be achieved.

Aqueous solutions containing calcium and carbonate ions can be applied to a fiber network, after forming, to precipitate calcium carbonate filler in paper. Selin and Hangaslammi /Selin and Hangaslammi 2002/ have patented the method of precipitating filler in a wet handsheet of fibres. The patent documentation does not contain any results. The chemicals used to precipitate calcium carbonate in the present study are different from those suggested by the inventors in their patent.

In this study (Publication I), a preliminary study was made to study the fast crystallisation of calcium carbonate from aqueous solutions in a paper network after forming. Aqueous calcium and carbonate ionic solutions were sprayed into a fiber network, containing an equal mixture of pine and birch fibres, at three different stages: after forming, pressing and drying. Mechanical pressing, of handsheets after spraying, assists to permeate the solutions inside the network and to expel them from the handsheets.

We compared the handsheet properties of calcium carbonate filler incorporated into a web of fibres, by precipitation or attaching of ground calcium carbonate (GCC), and conventionally formed standard laboratory made PCC-filled reference handsheets.

2.2 Experimental

Materials and methods

The pulps used were bleached kraft pulps from Finnish pulp mills made from pine (*Pinus silvestris*), spruce (*Picea abies*) and birch (*Betula pendula/pubescens*). The softwood pulp was a mixture of pine and spruce in a 2:1 ratio and the hardwood pulp was made from birch.

Identical mixtures of bleached softwood and hardwood kraft pulp were refined in a PFI mill for 3000 revolutions. Precipitated calcium carbonate[1] filler was added to the reference handsheets.

In the precipitation method, initial tests with calcium chloride and sodium carbonate solutions to precipitate calcium carbonate resulted in yellowing of handsheets. Therefore, the calcium carbonate filler was formed through a reaction between solutions of calcium chloride ($CaCl_2$) and ammonium carbonate ($(NH_4)_2CO_3$). At higher concentrations, due to saturation in solubility, ammonium carbonate was replaced with a solution of ammonium carbonate and sodium carbonate (Na_2CO_3). In the web spraying method, the wet web was hand-sprayed with GCC dispersion and cationic polyacrylamide (PAM-0.025%) polymer.

Filler was applied at three different wet web consistencies: after forming, pressing and drying, represented by precipitation (p) at the respective consistencies, p20, p45 and p98, as shown in Fig. 4. Calcium carbonate was precipitated by spraying $CaCl_2$ and $(NH_4)_2CO_3$ solutions onto the wet fibrous web and dry paper. After spraying, the sheets were treated as follows: 20% sheets were MTS sheet-pressed and drum-dried; 45% sheets were standard pressed and drum-dried; 98% sheets were drum-dried.

In web addition of filler, a ground calcium carbonate dispersion (denoted as GCC spray in Fig. 4) was sprayed onto both sides of a wet web at 20% web consistency, after forming. The wet web sheets were pressed with an MTS sheet press to a solids content of approximately 40%. Then, the sheets were sprayed with cationic PAM (C-PAM), and dried in a drum dryer.

Handsheets with a grammage of 80g/m^2 were formed in a laboratory sheet mould, according to ISO 5269-1:2005 and conditioned at 23 ºC and 50% RH in compliance with ISO 187:1990. The sheets were tested according to standard methods (Appendix). Reference sheets were formed with the addition of retention aid (Bentonite (2500g/t) and C-PAM (250g/t)) to the stock suspension. Polymer and bentonite were added in series followed by 30 seconds and 10 seconds mixing respectively, with air. Zero filler sheets were formed without filler addition.

[1] Precipitated calcium carbonate, with the trade name FS-240 and an average median particle size of 2.4µm, was supplied by Huber Oy, Finland.

2.3 Results and discussion

Preliminary experiments with web addition of filler showed that polymer treatment after filler addition is essential for preventing dusting of filler from the sheet. Negatively charged of fibres and GCC repulse each other and hence, cationic polymer was required to bind GCC to the fibres. We used the widely used retention aid in papermaking, C-PAM, dosed in minimal amount as determined during the initial trials.

In the web precipitation experiments, calcium carbonate precipitation using sodium carbonate and calcium chloride solutions resulted in yellowing of sheets probably due to the exothermic nature of the precipitation process. Further tests with ammonium carbonate or a mixture of ammonium and sodium carbonates as the ionic solutions for carbonate anion did not result in yellowing of paper and hence, they were used as anionic solutions.

The characteristics of the filler on the formed sheet were analysed using scanning electron microscopy, SEM (Publication I). In the web precipitation method, the filler is scattered as dense lumps through the sheet, and precipitated almost entirely on the surface of the fibres. In the studied web precipitation process, the filler agglomerated into larger and denser single particles of different sizes. In the web spraying of filler, patches of filler particles were in close contact and these filler particles were spread across the surface of the sheets.

Figure 4 illustrates the strength and optical properties of the sheets containing calcium carbonate filler added by different methods. The precipitation of calcium carbonate

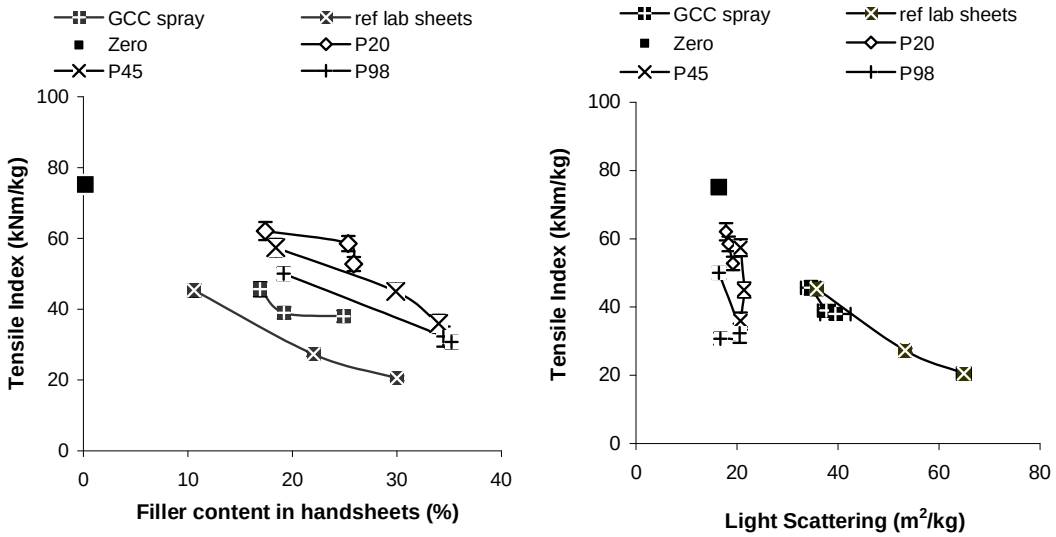

Figure 4 Tensile index development as a function of filler content and light scattering for different methods of filler addition to a wet web of fibres and reference samples. Abbreviations used: GCC spray – web addition of filler, ref – conventional addition of filler, P20, P45 and P98 – precipitation of filler using two solutions after forming, pressing and drying respectively, Zero- no filler addition.

gives clearly the highest tensile index for the paper. The GCC web spraying shows an initial decrease in tensile with the addition of filler. Increasing the filler content in web spraying above 20% has little effect on the tensile strength reduction in the

sheets. The reference samples show an approximately linear decrease in the tensile strength of paper plotted against the filler content.

The optical properties of handsheets show the opposite trend compared to the strength properties of paper. When tensile strength is plotted against light scattering, as shown in Fig. 4, precipitation onto the wet web lowers light scattering in comparison to control tests involving conventional filling. Also, wet web addition does not enhance the light scattering of paper. On the other hand, tensile strength decreases approximately linearly with an increase in light scattering for the reference sheets.

In the reference sheets, the presence of filler between the fibres interferes with the fibre-to-fibre bonding, and hence decreases the tensile strength with increasing filler content. In web spraying, filler penetrates into the top layer of the network in the wet pressed handsheets. This affects the bonding, showing an initial decrease in the tensile index of paper. Further addition of filler does not seem to have any effect on the penetration depth of filler into the handsheets, and hence the tensile index remains almost constant. In wet web spraying, the filler does not penetrate into the handsheets to any significant extent. On the other hand, accumulation of filler on the sheet surface results in optical crowding, and hence, the light scattering is distinctly lowered /Middleton, et al. 1994/. In this study, the tensile strength is highest for handsheets to which precipitated filler has been added owing to the scattered presence of aggregated filler between the fibres. The precipitation method and the corresponding pigment particle properties do not appear to have any significant disturbing effect on the fibre-to-fibre bonding in paper.

One of the goal of the experiments was to obtain an even distribution of filler, by web precipitation and web addition of pigment, through the thickness direction of paper. However, in both approaches the goal of uniform filler distribution was not achieved. This might be due to insufficient pressure to force the movement of the components after their application onto the fibre network or the narrow size of pores preventing the permeability of GCC inside the network.

2.4 Conclusion

The results of the preliminary study on introducing a filler into the wet web of paper showed that, under the studied experimental conditions, the handsheets had higher tensile strength and lower light scattering compared to reference samples. Web precipitated calcium carbonate was agglomerated while web application of calcium carbonate resulted in optical crowding of the pigment. However, in our study uniform filler distribution in the z-direction of paper was not achieved and filler characterestics were not optimised in this study.

On the other hand, precipitating calcium carbonate into a refined pulp suspension was assumed to have the same effect as wet web addition of filler due to the higher probability of retention of a PCC-cellulosic fibrillar network during the forming of paper. Hence, the continued research was focused on PCC-cellulosic fibril composite fillers.

CHAPTER 3

3.1 In-situ precipitation of calcium carbonate pigments in cellulosic pulp suspensions and their effect on fine paper properties

Different approaches have been proposed to increase filler contents in paper without impairing product quality. Lumen loading, proposed by Green, et al. aims to hold filler exclusively within the lumens of fibres /Green 1982, Middleton and Scallan 1985, Petlicki and van de Ven 1994/. This gives higher fibre bonding than conventionally filled sheets. A modified approach to lumen loading has been suggested in order to make it an industrially viable process /Middleton, et al. 2003/. Allan and co-workers /Allan and Negri 1992, Allan et al. 1998/ precipitated calcium carbonate in-situ by treating pulp successively with calcium chloride and sodium carbonate ionic solutions. Klungness /Klungness 1994/ developed a method to form PCC in a pulp refiner. Besides calcium carbonate, methods have been developed for incorporating aluminium /Siven and Manner 2003, Chauhan et al. 2007/ and magnetic (Rioux et al.1992, Zakaria et.al. 2004_a, Zakaria et.al. 2004_b) compounds inside the fibres. Pre-flocculation of filler /Mabee and Harvey 2000, Hak-Lae 2006, Holm and Manner 2001/ and co-flocculation of filler and fines /Gavelin 1998, Lin et al. 2007/ were examined to determine the feasibility of scaling up these processes as a means to increase the filler content in paper without impairing paper quality. Superfilled paper structures with a maximum filler loading of 90% were obtained by cationic wet end starch addition, as reported by Lindström and Floren /Lindström and Floren 1984/. Recently, Silenius /Silenius 2002/ has studied composites made from in-situ precipitation of PCC onto pulp fines.The product was termed as superfill. In his study, chemical pulp fines and heavily refined pulp, with high proportion of fines, were used as substrates in the lab work and pilot experiments. Higher retention, improved strength and optical properties of paper and cost savings were reported as the merits of using superfill filler.

Thus, a composite calcium carbonate material with potential use in papermaking can be formed by the precipitation of calcium carbonate (PCC) on top of cellulosic fibres and fibrils. There are many open questions about the production, use and potential benefits of these filler-fibre complexes. The objective of the present study was to produce various composite PCC pigments by the following methods: A. Using different pulps; B. Modifying the pigment crystal habits; C. Refining lime (calcium hydroxide) together with pulp, and subsequently precipitating calcium carbonate. The different PCC-pulp complexes were characterised and their effect on the production, printing paper quality, and print rub fastness were studied.

This chapter contains a summary of publications II, III, IV and V. Publications II, III and V are summarised as three studies as reported here and enumerated in Table III. Publication IV is referred to in the results and discussion, Section 3.4.3.

Table III Summary of studies described below and their related publications.

Study	Publications	
1	Effect of pulp substrate	II
2	Influence of PCC morphology	V
3	Refining pulp and calcium hydroxide together	III

3.2 Experimental

PCC precipitation experiments with different pulp suspensions were carried out in three studies, focussing on the following:

i. Effect of non-wood and wood pulp substrates on the precipitation of calcium carbonate filler and its performance in fine paper

ii. Effects of precipitated calcium carbonate crystal habits on the co-precipitation of PCC with pulp fibres and its influence on printing and writing paper production and quality

iii. Refining pulp and calcium hydroxide together and subsequent carbonization to obtain precipitated calcium carbonate and its impact on copy paper properties

3.2.1 Materials

Effect of pulp substrate

One of the principle variable in microfibrillation is the choice of the pulp. Pulps with different chemical and morphological characterestics will produce different levels of fibrillation. This can be used as an effective tool to improve the adhesion of PCC and strength-light scattering relationship of the fine paper. Thus, five different refined chemical pulps were used to precipitate composite calcium carbonate filler: pine, birch, mixed Indian hardwood (HWI), bagasse and rice straw pulp. The pine pulp was a 1.5:1 mixture of pine and spruce, while the HWI pulp was a 2.3:1 mixture of eucalyptus and casuariana species. The pine and birch pulps were never-dried, the other three pulps dried. The pine, birch and HWI pulps were kraft pulps, while the bagasse and rice straw pulps were produced by the soda pulping method.

The five pulp substrates were refined in a Masuko refiner (supermass colloider®) – a special grinder which imparts high external fibrillation to the pulps – to produce a suspension of fines and externally fibrillated fibres. The gap between the stones was adjusted to 160 µm, and the treated pulp was discharged by centrifugal force. The refining was carried out twice by recirculating the pulp suspension.

Based on Bauer-McNett screening of the unrefined pulps and the pulps refined by ultra-fine friction, the pine pulp was found to have the highest and rice straw pulp the lowest percentage of long fibre fractions (Table IV). The amount of fines, denoted by the P200 fraction, was highest for rice straw pulp and lowest for birch pulp. The fines

fraction of bagasse pulp samples was higher than those of the pine, HWI and birch pulps.

The refined pulp substrates were mixed with slaked lime in a 1:1 ratio, and treated with carbon-dioxide to co-precipitate calcium carbonate composite fillers.

Influence of PCC morphology

ECF-bleached unrefined pine pulp obtained from a mill in southern Finland was ground in a Masuko refiner (supermass colloider®) to produce fines. Bauer-McNett analysis of the fines showed that 92% of the pulp fines passed through a 200-mesh screen. The consistency of the fines-PCC composite was in the range of 0.085% to 0.1%. The fines were mixed with slaked lime to co-crystallise PCC, composed of 2 PCC:1 fibrils, with various crystal habits.

Table IV Bauer-McNett classification of unrefined and refined pulp samples used in co-precipitation of composite fillers.

Pulp	Characteristics	Screen mesh >30	30-50	50-100	100-200	<200
Pine	unrefined	78.5	12.2	6.5	2.6	0.3
	refined	13.0	14.8	16.8	13.9	41.6
Birch	unrefined	1.8	56.4	26.2	5.5	10.1
	refined	1.8	26.3	30.7	13.3	28.0
Bagasse	unrefined	9.7	21.8	31.3	17.0	20.2
	refined	0.1	1.7	13.5	24.8	59.9
HWI	unrefined	0.1	39.4	30.8	7.7	22.0
	refined	0.1	14.6	33.5	14.0	37.8
Rice straw	unrefined	12.6	22.8	19.0	11.4	34.3
	refined	0.0	1.3	8.4	11.3	78.7

Abbreviation: HWI = mixed hardwood pulp (sourced from India)

Refining pulp and calcium hydroxide together

The pulp used to produce composite filler was a commercial never-dried bleached kraft pulp made from pine and spruce, provided by a Finnish mill.

Softwood pulp and calcium hydroxide equivalent were mixed to obtain a 2:1 mixture of PCC and pulp. This mixture was refined under the following conditions:

a) The mixture was refined in a Masuko refiner (supermass colloider®) with a stone gap of 160 µm. Samples were taken after 1, 3 and 5 passes through the refiner.
b) The mixture was mixed initially in a Hollander beater for 25 minutes and then beaten for 0, 15 or 30 minutes.

The freeness values of the pulp samples are shown in Table V.

Table V Freeness of refined pulps.

Refiner	Masuko	°SR
Masuko	M – 1 pass	21
	M – 3 pass	76
	M – 5 pass	86
Hollander	H – 0 min	13
	H – 15 min	19
	H – 30 min	46

Samples were also produced by refining the softwood fibres under conditions similar to those described above, but in the presence of conventionally produced PCC in the ratio of two parts filler to one part fibres. Reference samples were produced by refining pulp without any PCC or Ca $(OH)_2$ present. Thus, the experiment consisted of six refining conditions and three methods of filler addition – in-situ precipitation, refiner addition and conventional addition.

3.2.2 Handsheet forming

Effect of pulp substrate

A mixture consisting of equal proportions of never-dried commercial bleached softwood pulp and hardwood pulp, refined in a Valley beater to a freeness of 30 ˚SR, was used as the base pulp furnish for this study. Dual retention aids consisting of bentonite (2500g/t of paper) and cationic polyacrylamide[2] (C-PAM; 250g/t of paper) were used. Commercial scalenohedral precipitated calcium carbonate[3] with an average mean particle size of 2.7 µm (FS-270) was used in the preparation of reference handsheets. The preparation of composite and reference handsheets, with a reference PCC and a reference PCC-pulp fibril mixture, is detailed in Publication II.

All the sheets having a grammage of 80g/m^2 were formed with the same base pulp furnish and retention aid additions on a moving belt former (MBF). The MBF simulates, in certain aspects, the forming section of a paper machine /Räisänen 1998/.

Influence of PCC morphology

Refined pine softwood (23 ˚SR) and birch hardwood pulp (18 ˚SR) in a 30:70 ratio were used as the base furnish. C-PAM (250g/t paper) was used as the retention aid in forming handsheets. No other additives were used. Conventional fillers, provided by J.M. Huber, produced under similar conditions as composite PCC's were used in the reference experiments.

Composite and reference handsheets (80g/m^2) were produced in a standard handsheet mould with the addition of retention aid. The samples were pressed twice in a material testing system (MTS) press at an impulse of 3.3 mPa/0.02s with two blotting papers on each side. The handsheets were dried under standard conditions in a drum drier.

Refining pulp and calcium hydroxide together

Composite and reference fillers were added to a base furnish of birch pulp (SR =23˚) to produce handsheets with a filler content in the range of 10-30%. In conventional addition, the refined softwood was added to the base furnish, followed by filler addition just before the making of handsheets. Retention aid was added to the stock suspension containing the base furnish, refined softwood pulp and filler. Sheets with a grammage of 80 g/m^2 sheets were formed on a moving belt former (MBF). The sheets were pressed with a material testing system sheet press (3.7mPa/300s), and dried on a drum drier. The results were normalized to 20% filler content.

3.2.3 Testing

The handsheets were tested according to standard methods (Appendix).

[2] Provided by Ciba Speciality Chemicals company
[3] Supplied by Huber Engineered Materials company

The first-pass retention was calculated as a percentage of the PCC retained in the handsheets to the total amount present in the stock suspension. For composite fillers, the total filler was measured from the whole composite sample, by ashing at 550°C, to compute the amount of filler added to the base furnish.

For calcium carbonate filler precipitated onto the surface of fibrils, the specific surface area was determined by oxidizing the cellulosic fibres at low temperature (300 ºC) followed by oxidation for 1 hour at 500°C. The specific surface area of the ash residue and reference PCC was determined with the Brunauer-Emmett-Teller (BET) nitrogen adsorption method. The measurement was carried out with a Micromeritics Gemini 2375 apparatus.

The particle size distribution was determined by sedimentation of the ash residue with a Sedigraph 5100. Ashing was used to assess the primary particle size distribution properties of the filler. The functionality of the filler, especially when combined with fibre, will additionally depend on the structures formed, including agglomerates and/or composites. The role of particle size in this case needs to be viewed in close relation with the microscopic analysis of composite particle structures. From the log-normal graph of the particle size vs cumulative mass percentage the median particle size (MPS) is determined. MPS represents the equal division of the mass of all particles present in the suspension. The particle size "75/25 ratio" is calculated from the Sedigraph as the measured value of the pigment particle size measured in microns at the 75 percentile, divided by the particle size measured in microns at the 25 percentile. The 75/25 ratio is a measure of the breadth of the particle size distribution, and lower and higher values of the 75/25 slope indicate that the particle size distributions are narrower and broader, respectively.

Attached filler in the composite was determined as follows: A 2-gram sample of filler and pulp was washed 8 times at 800 rpm in a dynamic drainage jar (DDJ) fitted with a 100-mesh screen. The filler content of the material left on the screen determined by ashing at 500°C is the attachment value. Experience has shown that this amount of washing is sufficient to remove all free filler from the pulp suspension. Thus, if filler is added to fibres in a conventional way, the attachment value is close to zero. However, the attachment level increases, if PCC is precipitated in situ or thoroughly mixed with pulp fibres, due to diffusion into the lumens or adsorption onto the fibre surfaces. filler to adsorb to the filler surfaces.

3.2.4 Absorption and structural properties of handsheets

Influence of PCC morphology

The handsheets were printed on HP LaserJet (4350dtn) and inkjet (Epson stylus C44UX) printers. The density and gloss were measured using Viptronic 4-794 and Vipgloss-I (4 -778) devices, respectively.

Printing ink rub resistance was tested with a PATRA print rub tester, using VTT test method 4716-94, with 2696 g weight and 200 disc revolutions. In PATRA rubproofness tester, rubbing occurs when a printed sample eccentrically rotates against unprinted paper under a weight. The rotation velocity of the device is 60 rpm. Pressure and smearing surface can be varied. Also the cover substrate and smearing part can be varied. Smearing time is freely selectable too. Smearing in the unprinted paper is usually measured by a densitometer.However, in our analysis with the

handsheets containing composite filler, density values were low and out of range of the densitomer. Hence, we measured whiteness of handsheets to compare the smearing intensity in the unprinted paper according to ISO 11475:2004.

3.3 Precipitation of calcium carbonate in pulp suspension

Equivalent amounts of calcium hydroxide suspension were added to the fibrillated pulp suspension, in order to obtain 2:1 and 1:1 PCC- pulp fibril mixtures, which were then carbonated to co-crystallize PCC's with colloidal-, rhombohedral- and scalenohedral-type structures. The carbonation was carried out using a mixture of 20% CO_2 and 80% air. The progress of the reaction was monitored by conductivity measurement, as shown in Fig. 5 for the production of a 2:1 colloidal composite filler.

PCC morphology was controlled through crystallization of intermediary phases as described by Yamada and Hara /Yamada and Hara 1987/. This study details the phase changes that occur over a period of time during the carbonation process, reaction of milk of lime and carbon dioxide. The reaction was monitored using electrical conductivity of milk of lime and pH. The formed crystals were analysed for their characteristics using X-ray diffraction, thermogravimetric and tunneling electron microscopic (TEM) studies.

To illustrate the observed changes in conductivity and pH during the composite PCC, colloidal PCC composite crystallisation is shown in Fig. 5. The following mechanism can be proposed, similar to precipitation of PCC from lime /Yamada and Hara 1987, Carmona et al. 2004/, to explain the changes in the conductivity of lime during the precipitation of colloidal composite PCC.

1. In this process, in the first descending curve of the conductivity value is related to the surface precipitation of tiny amorphous calcium carbonate (ACC), which partially covers the surface of lime particles inhibiting its dissolution. Subsequently, when the density of the particles is high enough, the inter-particle interactions become important and they aggregate in a line, probably by the polarization of the particles. This aggregation can be seen on the surface of the fibrils in Fig. 6.
2. In the next zone, with ascending conductivity, the crystallisation of ACC into chain-like calcite proceeds, being accompanied by its desorption from the lime surface, which enables a further dissolution period of $Ca(OH)_2$.
3. With the growth of chain-like calcite, the solution is enriched with calcium and carbonate ions while $Ca(OH)_2$ disappear. The conductivity starts to decrease until the complete consumption of the calcium and carbonate ions.
4. In the last ascending curve, some of the inter-particle material in the chain-like aggregates probably dissolve and separate into individual particles which grow into nanometrically sized calcium carbonate.

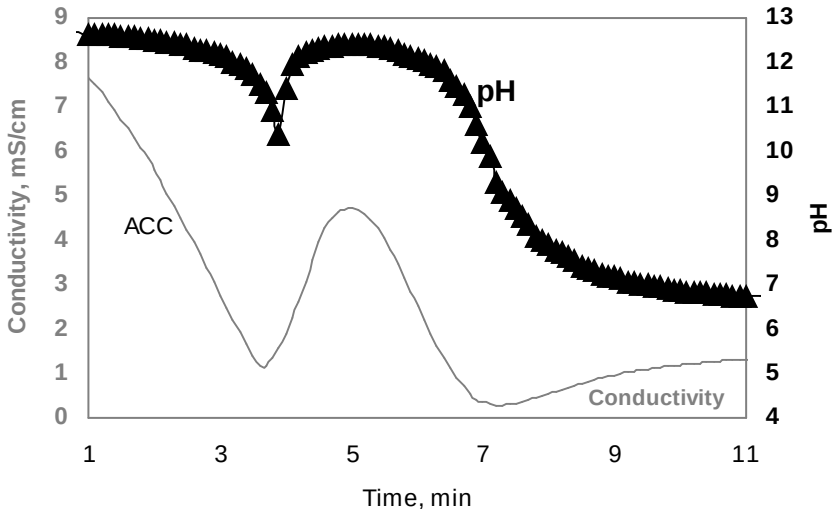

Figure 5 Parameters observed during the crystallization of composite calcium carbonate filler with colloidal morphology. Abbreviation: ACC – Amorphous calcium carbonate.

On the other hand, due to differences in the nucleation mechanism, rhombohedral PCC was obtained through amorphous calcium carbonate (ACC) and partially carbonated basic calcium carbonate (BCC), as shown below.

$$Ca(OH)_2 \xrightarrow{CO_2} ACC \xrightarrow{CO_2} BCC \xrightarrow{CO_2} \text{Rhombohedral PCC}$$

Scalenohedral PCC was precipitated onto cellulosic fibrils in similar conditions as described in literature / Carmona et al. 2003, Meuronen 1997/.

3.4 Results and discussion

3.4.1 Filler characteristics

Effect of pulp substrate

The properties of the composite filler formed with the different pulps are shown in Table VI. The solids indicate the percentage of dry matter in the sample. The total

Table VI Properties of composite filler formed in different pulp suspensions. BET refers to the specific surface area of attached filler. FS-270 is a commercially produced scalenohedral PCC.

Pulp type	Solids (%)	Total filler (%)	Attached filler (%)	BET (m^2/g)
Birch	3.5	46.1	21.4	6.1
Pine	3.1	44.4	19.5	8.3
Bagasse	4.3	42.7	9.1	6.2
HWI	2.8	46.9	11.7	6.4
Rice Straw	4.2	51.5	11.0	20.9
Reference	18.0	100	-	6.4

Note: Reference PCC does not contain any fines, and hence, attached filler is not indicated.
Abbreviation: HWI = mixed hardwood pulp (sourced from India).

filler represents the percentage of PCC in the fines-PCC composite. The attached filler is the amount of PCC which is not removed from the pulp after thorough washing in a dynamic drainage jar, as enumerated in section 3.2.3. It shows that the filler attachment to the fibres and fines is higher with non-dried pine and birch pulps than

with dried bagasse, rice straw, and HWI pulps. Filler specific surface area (BET) measurements show that the rice straw filler is a high-surface-area product, while other composites have surface areas similar to a commercial grade reference PCC (FS-270) often used in office papers.

Influence of PCC morphology

The composite c-PCC consists of precipitated nano-crystals aggregated into ellipsoidal shapes, as shown in Fig. 6. The precipitation occurs at random sites mostly on the end of fibrils and, hence, the fibrils are partially covered with calcium carbonate fillers. The particle size of the primary composite c-PCC particle is less than 100nm.

The composite r-PCC's are found in clusters forming a pearl necklace structure with the fibrils, as shown in Fig. 6 right-hand side micrograph. Some fibrils are covered by the PCC particle surface. In addition, films of microfibrils covering PCC surfaces are seen in the micrographs. The particle size of composite r- PCC's is below 2 µm.

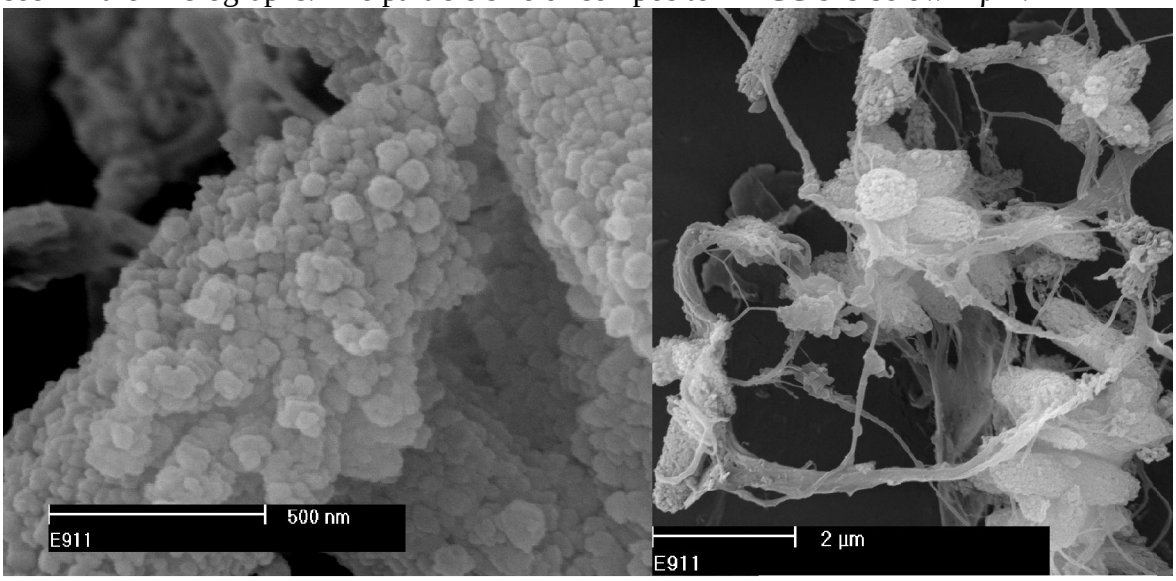

Figure 6 Colloidal precipitated calcium carbonate composite (Acronym: composite c-PCC).

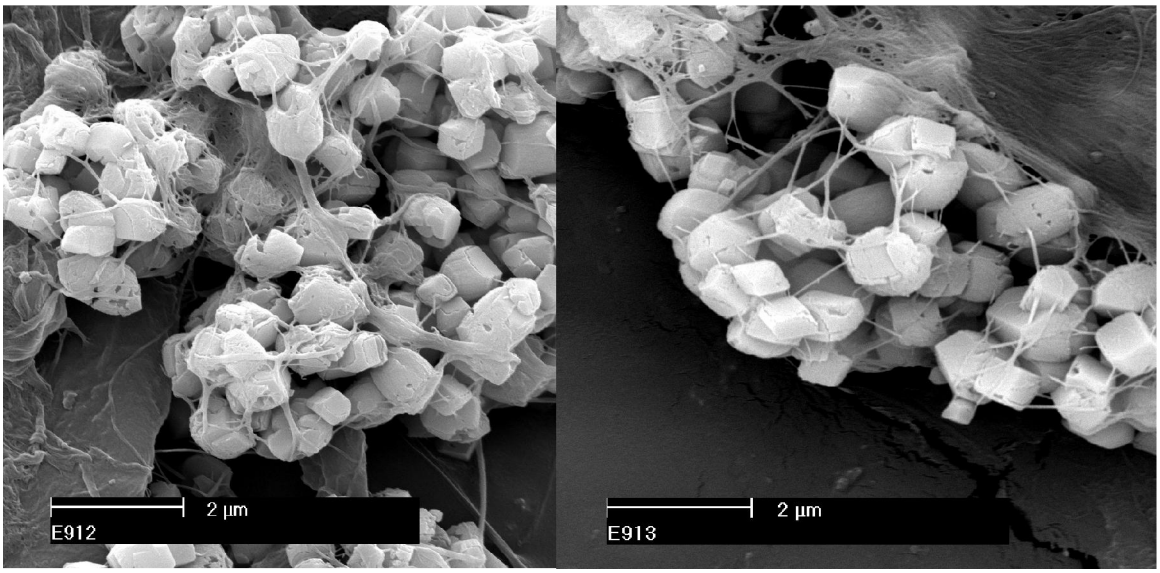

Figure 7 Rhombohedral precipitated calcium carbonate composite (Acronym: composite r-PCC).

According to Alince, the scattering ability of a pigment is a function of its refractive index and size /Alince 1989/, and in the case of agglomerates, also the particle spacing. Unbonded fibre surfaces contribute to light scattering due to debonding and its micrometre dimensions /Alince and Lepoutre 1985/. The SEM picture in Fig. 7, right-hand side, shows that the width of some of the fibrils connecting the PCC's is below 200nm, and hence, these fibrils may not contribute to improving the light scattering of paper.

Fig. 8 shows the structure of the composite s-type PCC, formed under the experimental conditions similar to that of reference s-PCC. Due to low solids and the presence of fines in the suspension, the precipitate appears to have ellipsoidal form and is not structured, in contrast to the structured reference s-PCC filler. The fibrils appear to disrupt and inhibit the growth by covering the particle surfaces, as shown by the dark voids in the picture. Therefore, the particle size of these precipitates is lower than that of the reference PCC. The precipitates are intertwined in a network structure. Among the studied crystal habits, composite s-PCC particles crystallised more evenly on the surface of the fibrils. In contrast, c- and r-PCC were agglomerated and aggregated on the fines surface and thus, had lower surface coverage.

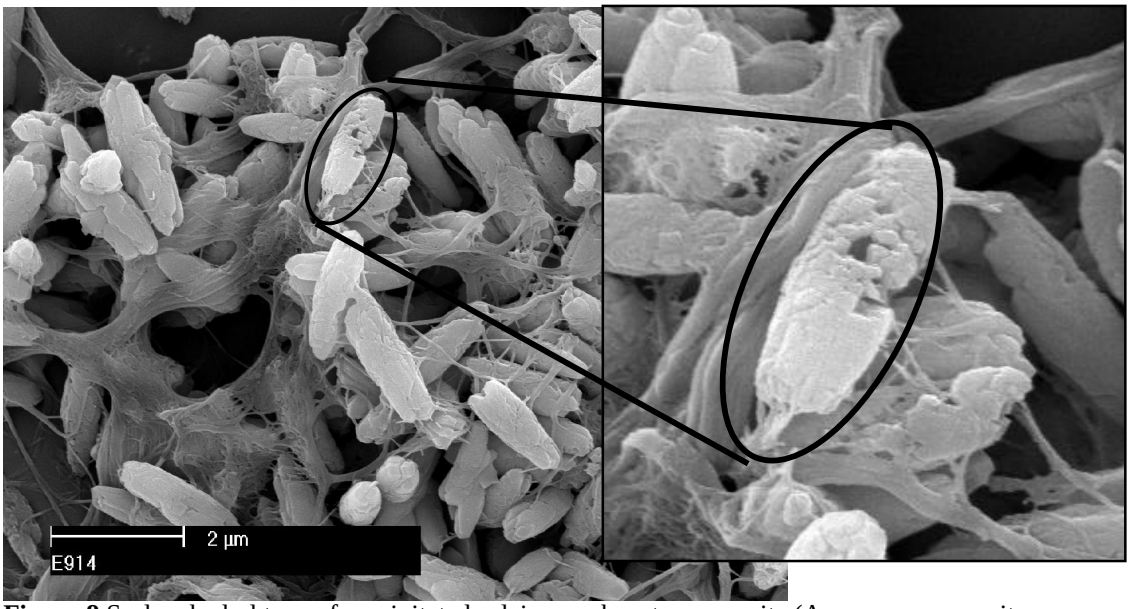

Figure 8 Scalenohedral type of precipitated calcium carbonate composite (Acronym: composite s-PCC).

Fig. 9 illustrates mixing of fines and reference structured s-PCC filler, with a mean particle size of 2µm. The fibres were refined to microfines and subsequently, calculated amount of s-PCC filler was added to this suspension and mixed thoroughly for 5 minutes. This fines-filler mixture was added in required amounts to a copy paper furnish to form reference handsheets. From the micrographs, we observe that the filler is embedded into the fines network and partially covered by the fibrils. During mixing, the fibrillar network is pierced by the PCC particles, as seen on the right-hand side micrograph of Fig. 9. This will prevent the fibrils from merging together during drying of the handsheets.

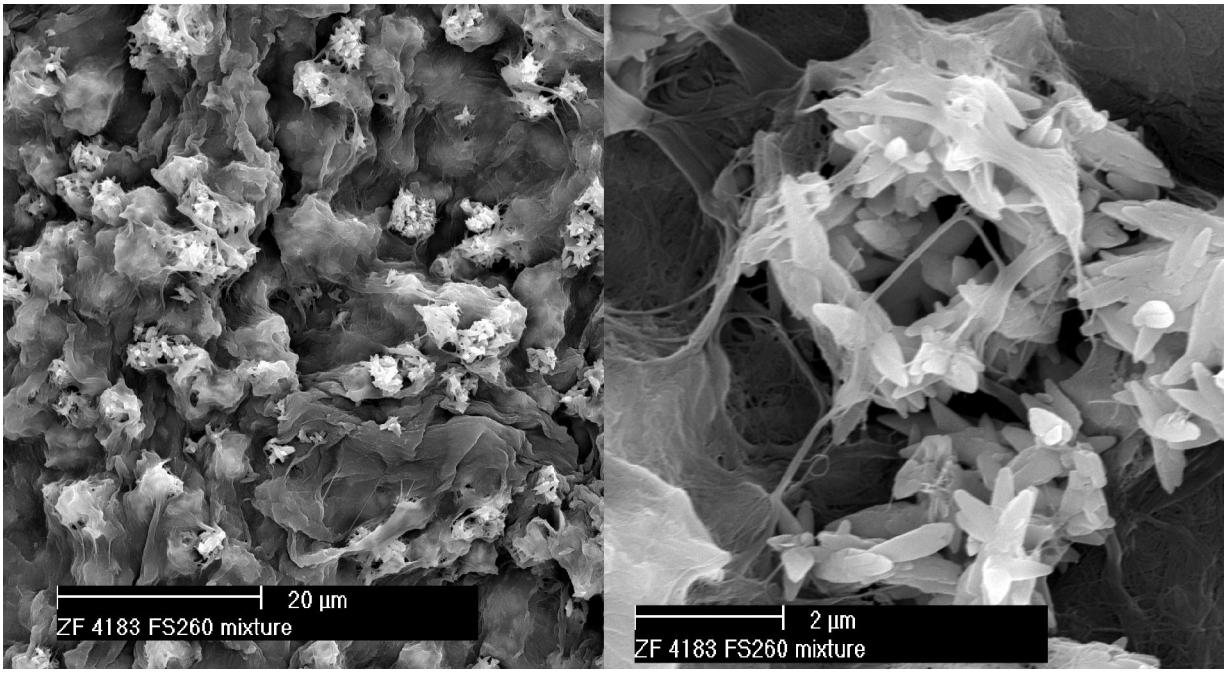

Figure 9 Scalenohedral PCC mixed with fines (Acronym: reference s-PCC+fibril mixture).

Refining pulp and calcium hydroxide together

The properties of the composite samples are shown in Table VII. For both refiners, the attached filler increases with a higher degree of refining. Refining is believed to increase PCC attachment because it increases the cellulose surface area available for precipitation and also because it is more difficult to wash filler out of a more highly fibrillated network. All the precipitated filler samples have about the same surface area – around 10 m^2/g. This is somewhat higher than for the conventionally produced reference sample, but still in the range of ordinary fine paper PCC fillers. It is interesting to note that the refining has decreased the particle size of the composite filler somewhat compared to the unrefined one (H-0). This may be due to grinding of the lime in the refiner.

Table VII Properties of composite filler formed after milk of lime and pulp are refined together under different conditions.

Refiner	Composite Filler	Total filler content (%)	Attached filler (%)	BET (m^2/g)	MPS [µm]	75/25 ratio
Hollander	H- 0 min	61.6	11.6	11.0	2.27	8.92
	H- 15 min	63.0	12.4	10.7	1.15	4.29
	H- 30 min	63.0	19.0	11.5	0.98	2.28
Masuko	M- 1 pass	65.5	15.5	9.67	1.56	11.43
	M-3 pass	65.2	21.0	9.59	1.31	9.66
	M-5 pass	65.8	19.3	9.69	1.48	10.50
Reference	FR-180	100	-	5.1	2.62	1.8

Note: Reference PCC does not contain any fines, and hence, attached filler is not indicated.

The apparently wide particle size distribution (high 75/25 ratio) of the composite samples compared to reference, FR180, is not directly comparable to the value of pure PCC samples measured in a conventional particle size test. It is interesting to note that the particle size distribution of the Hollander-refined composite filler becomes

significantly narrower in refining. This indicates some changes in the filler distribution and state of agglomeration from refining the lime and PCC together.

3.4.2 Retention and dewatering

The first-pass retention of the different types of filler is shown in Fig. 10, as determined in studying the influence of PCC morphology. The PCC-microfines composite filler gives higher retention than the reference PCC because of the higher retention of fines in the presence of retention aid, C-PAM. The colloidal c-PCC's were found to have the highest first-pass retention, which is probably due to the PCC morphology (Fig. 6) and agglomeration. The retention of particles has been found to increase with an increase in particle size, aggregated pigments, platy type filler and coarse particles /Bown 1996/.

The mixture of reference PCC's and microfines has a higher retention than only reference PCC's but lower than the composites. Mixing of filler with fines traps the filler into the fines network (Fig. 9), resulting in higher retention than with addition of reference PCC by itself (Lin et al. 2007).

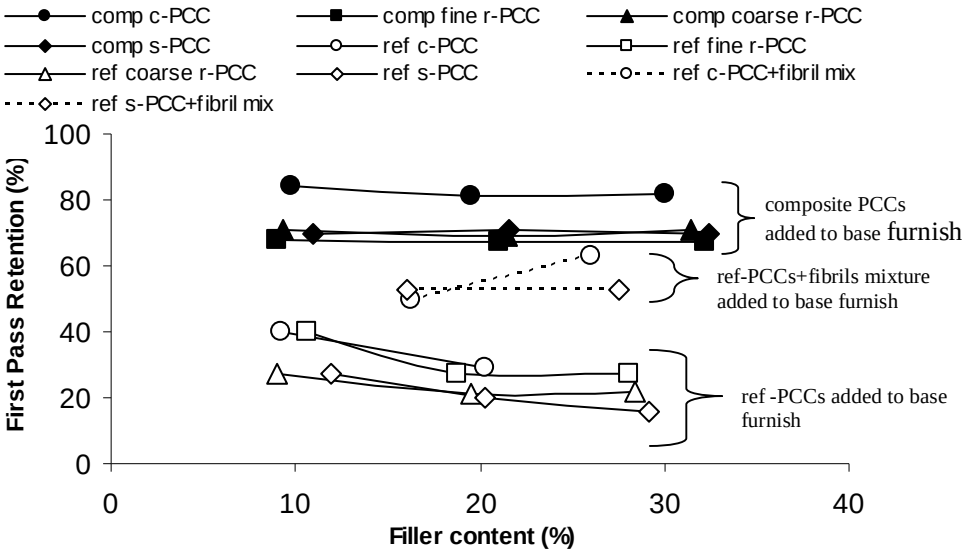

Figure 10 First-pass retention of composite PCCs, ref-PCC's and ref-PCCs+fines mixture. Abbreviations: comp = composite; ref = reference; c= colloidal PCC; r = rhombohedral PCC; s=scalenohedral PCC; mix = mixture.

Dewatering of the handsheets with various fillers after the first press is illustrated in Fig. 11. It is seen that the reference PCC gives the highest dry solids with an increasing filler fraction in the paper. Mixing of fines with reference PCC significantly reduces the dry solids of handsheets after pressing. Among the reference fillers, structured s-PCC shows lower dry solids because of the water retention in the pores of the particles.

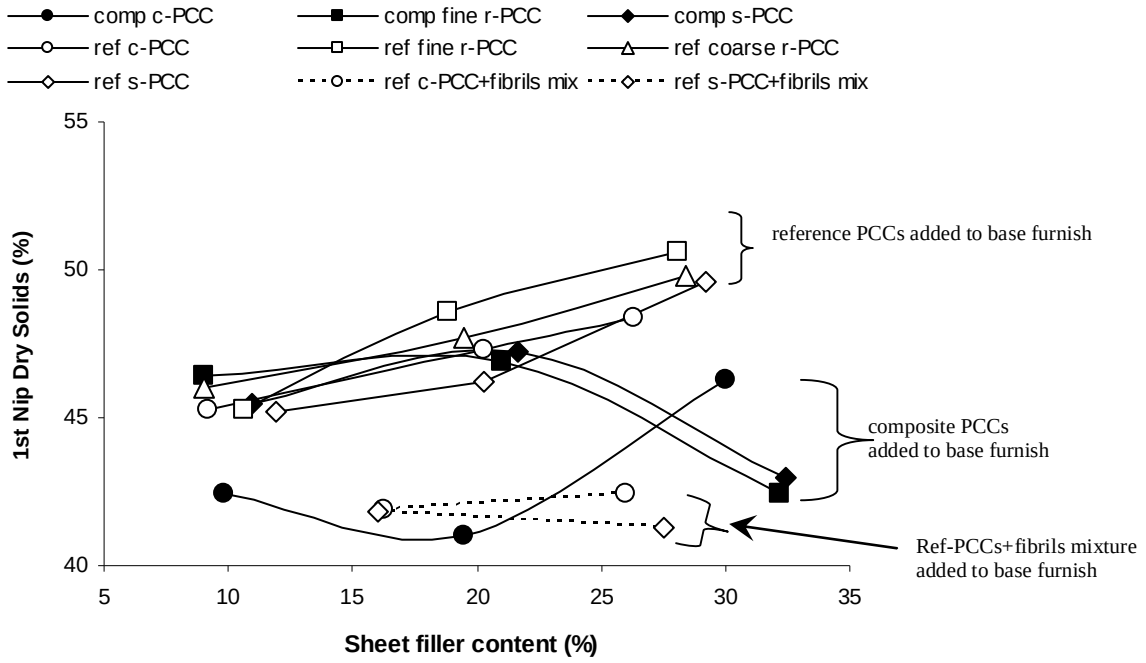

Figure 11 Dewatering of composite fillers, conventional PCC's and PCC-fines mixture handsheets at first press nip. Abbreviations: comp = composite; ref = reference; c= colloidal PCC; r = rhombohedral PCC; s=scalenohedral PCC; mix = mixture.

Among the composites, at a lower handsheet filler content, the composite c-PCC shows the lowest dry solids, probably due to the homogeneous distribution of fillers, leading to poor drainage. At higher filler contents, the drainage of colloidal fillers increased, possibly due to the expansion of the network structure. The expansion of the structure is confirmed by the increased bulk shown by the composite c-PCC filled handsheets. At high filler contents, greater than 20%, the drainage of composite s- and r-PCC samples decreases significantly, probably due to the higher amount of film-forming fines in the structure.

3.4.3 Paper properties

Paper properties, as determined in studying the influence of PCC morphology, are shown in Fig. 12. Fines addition, in the form of a PCC composite or as a mixture of filler and fines, increases the density of paper. In contrast to reference PCC filler, a composite filler containing kraft fines enhances Campbell's forces, and thus, aids in forming a dense network structure /Retulainen 1997/. Among the reference fillers, addition of s-PCC causes a significant increase in the air permeability and a decrease in density. Addition of reference c-PCC results in a minimal increase in the air permeability of paper.

Addition of fines improved the bending stiffness of handsheets, as shown in Fig. 12, due to stronger bonding and higher specific bond strength /Retulainen, et al. 1993, Häggblom-Ahnger 1998/. Addition of a mixture of reference PCCs and microfines gives the highest bending stiffness resistance. Addition of reference r- and c-PCC gives the lowest bending stiffness, which decreases with increased addition of filler.

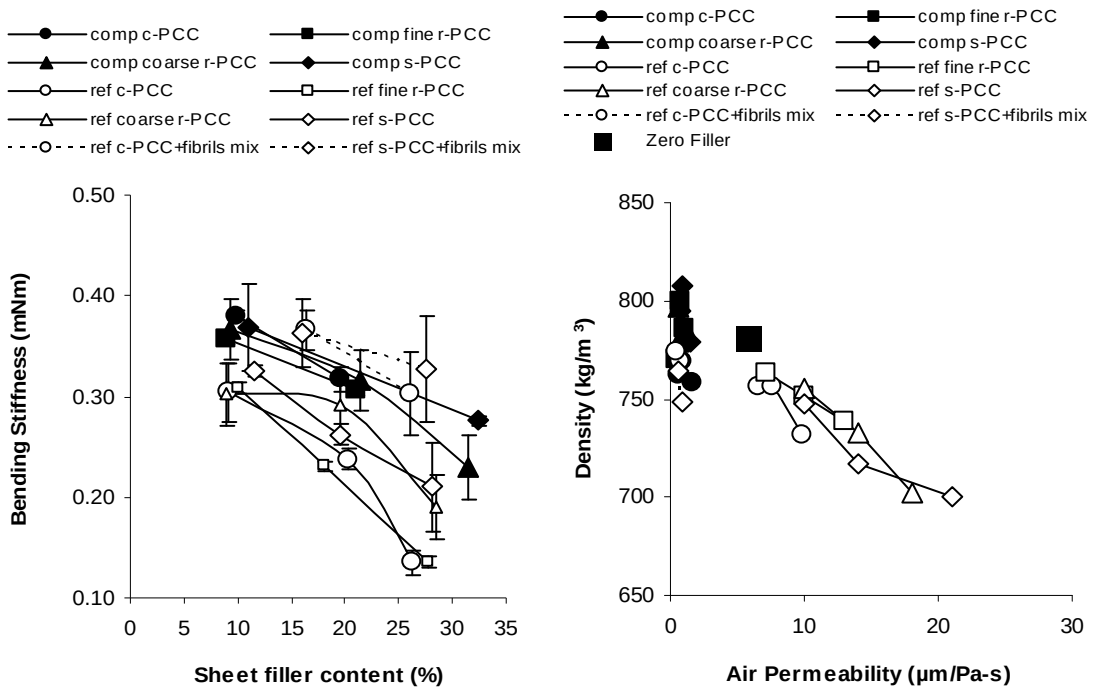

Figure 12 Impact of PCC filler loading, as a function of PCC particle morphology, on the structural properties of paper. Abbreviations: comp = composite; ref = reference; c= colloidal PCC; r = rhombohedral PCC; s=scalenohedral PCC; mix = mixture.

Comparing the internal bond strength and tensile index of various morphologies of PCC (Fig. 13), composites are found to give higher tensile strength than the reference fillers. These results correlate with earlier research findings /Xu, et al. 2005_a and 2005_b/, showing that fines contribute to strength by acting as a bridge that increases the bonding area in paper. Among composites, at all filler contents, papers filled with c-PCC and r-PCCs show minimum and maximum internal bond strength, respectively. Composite c- PCC imparts reduced tensile at low filler contents.

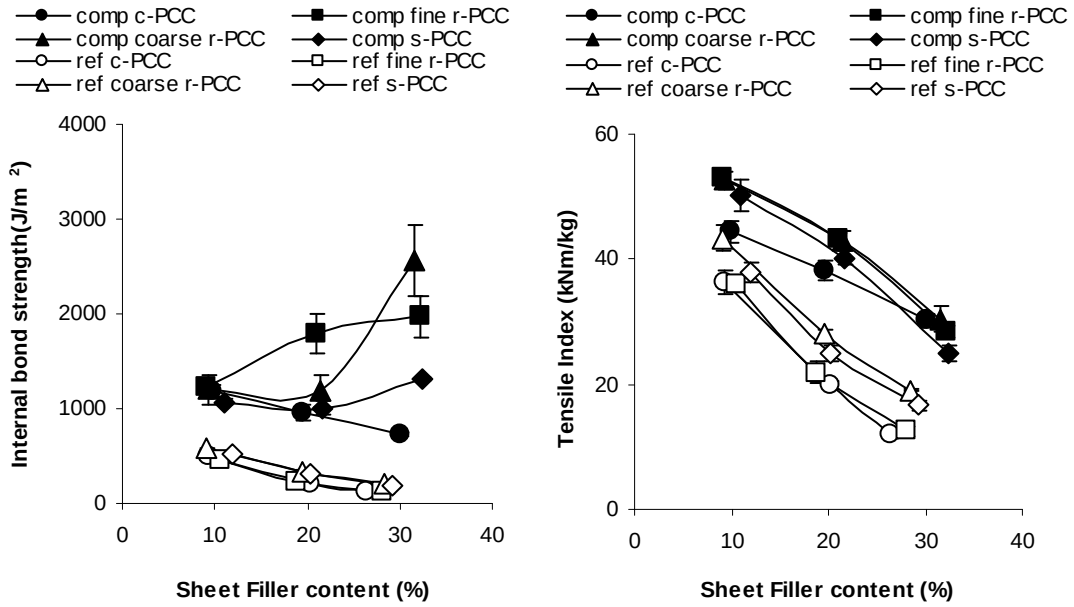

Figure 13 Comparison of the strength properties of handsheets as a function of filler amount for composite and conventional PCC filler with three different morphologies. For abbreviations, refer to Fig. 12.

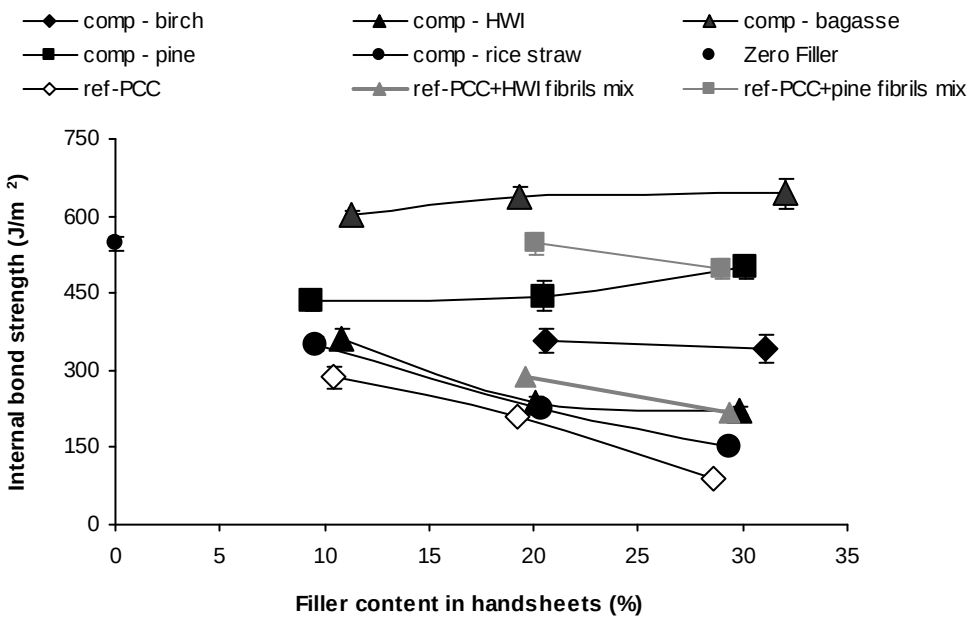

Figure 14 Internal bond strength of handsheets formed with composite and reference samples. For abbreviations, refer to Fig. 10; HWI – Hardwood mixture sourced from India. Abbreviations: comp = composite; ref = reference; c= colloidal PCC; r = rhombohedral PCC; s=scalenohedral PCC; mix = mixture.

In studying the effect of the pulp substrate, the z-directional bond strength was found to be highest with bagasse composite containing fine paper (Fig. 14). The out-of plane inter-fibre bond strength of bagasse composite filler is remarkably higher than that of the reference, and even better than for the zero filler added paper. Higher internal bond strength was obtained even when the amount of PCC was doubled in the PCC:fibril mixture, as seen from the results of publication IV. This might be due to the increased bonding caused by the short fibres and fines and the morphology of the bagasse pulp substrate. Srinivasa /Srinivasa 2000/ has reported a similar conclusion, stating that the higher strength shown by bagasse fibres is due to the increased bonding caused by the high swelling of refined bagasse pulp samples. Mayank and Singh /Mayanak and Singh 2004/ show that the relative bonded area of recycled bagasse pulp increases during refining, increasing the tensile strength of handsheets. Pine composite filler addition shows that the internal bond strength is higher than for other composites but lower than for the zero-filler reference. Thus, the increase in z-directional bond strength depends on the type of fibre and the characteristics of the fibre fractions in the pulp sample. Ref-PCC imparts the lowest internal bond strength to the handsheets.

In studying the effect of the pulp substrate, the handsheets with composite fillers were found to have the highest light scattering, as shown in Fig. 15. The light scattering and opacity of pine composite handsheets were distinctly higher than those of other filler composites. According to these results, the light scattering is dependent on the type of pulps used in co-precipitation of composite filler. Among the composite filler added handsheets, the pine and rice straw composites had the highest and lowest light scattering, respectively.

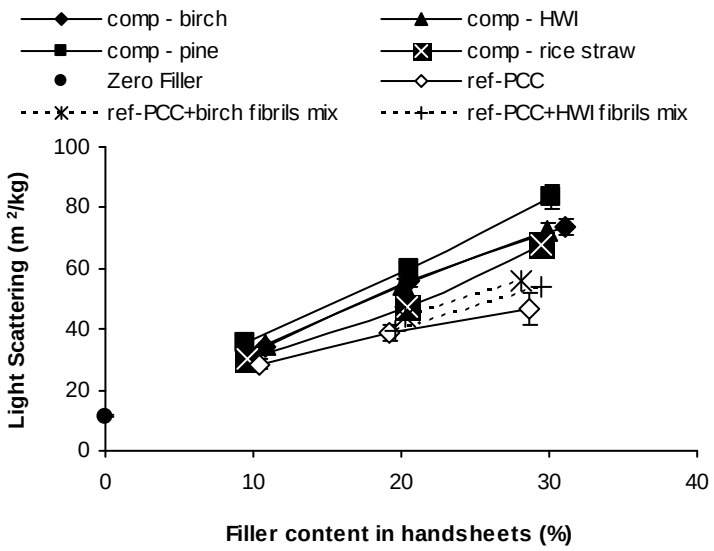

Figure 15 Effect of composite and reference filler addition on the light scattering of paper. Abbreviation: comp = composite; mix = mixture; ref = reference; HWI = Hardwood mixture from India.

Comparing the light scattering produced by composite fillers and reference blends, the composite material is found to give significantly better optical properties than a simple blend of PCC and fibrillated pulp.

In contrast to the findings of an earlier study (Fig. 15), the study of PCC morphology showed that composite and reference PCCs produce similar light scattering, as illustrated in Fig. 16. Silenius /Silenius 2002/ has noted that the light scattering of composite fillers depends on the particle size of the precipitated calcium carbonate particles. According to the present research, precipitation onto cellulosic fibres and fibrils can lead to a decrease in the surface area and particle size of the composite particles due to inhibition of crystal growth, as shown in Figs. 7 and 8 (Publication V). Also, the microfines with a size of less than 200 nanometers used in the PCC morphology study co-precipitations (Fig. 7) will not contribute to the light scattering of composite handsheets.

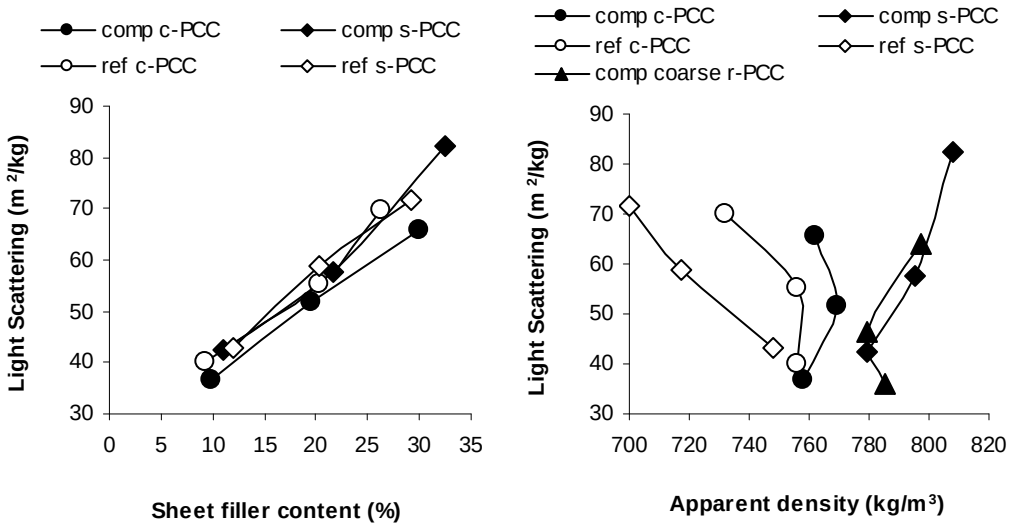

Figure 16 Impact of PCC particle morphology on the light scattering properties of composite and conventional PCC filled handsheets. Abbreviation: comp = composite; ref = reference, mix = mixture.

However, even with increased density, composite fillers impart light scattering similar to that produced by conventional reference fillers (Fig. 16). This is due to the higher number of small sized optical pores generated in the PCC composite network structure. The light scattering efficiency is directly related to the surface area associated with the optically active pores /Alince et al. 2002_a/.

Experiments with simultaneous refining of softwood pulp and calcium hydroxide, followed by carbonization, show that the light scattering of paper filled with the PCC composite increases as a function of refining (Fig. 17). It is notable that there is a significant improvement in light scattering from an addition level of about 43-45 m^2/kg up to 50-55 m^2/kg with normal or refiner addition to a lightly refined pulp refined to about 20 °SR. Refining to much higher levels will give only a slight improvement in light scattering. However, this must be weighed against the high refining energy consumption, capital requirements and potential dewatering problems with composites formed from a pulp that has been refined to extreme levels.

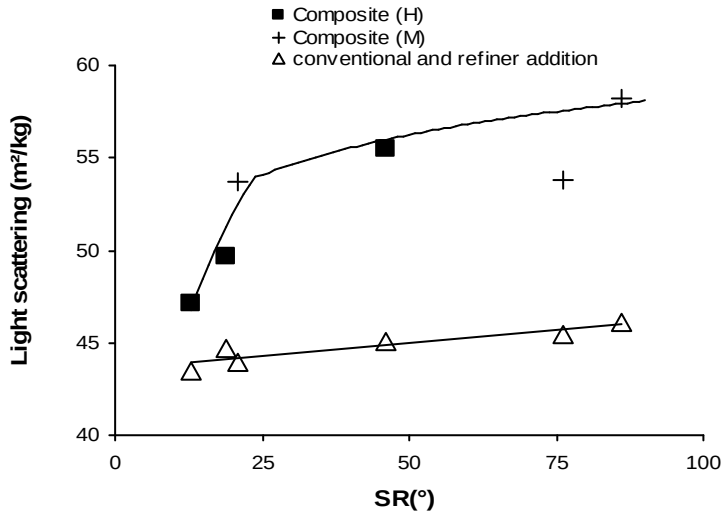

Figure 17 Light scattering of handsheets made with composite and conventional PCC samples at 20% filler content. Abbreviations: M-Masuko, H-Hollander.

A comparison of light scattering against tensile index for the composites produced by joint refining of pulp and milk of lime shows that the shift in the scattering-tensile curve of the handsheets is not much different from the effect of increasing the filler content in the reference samples, i.e., light scattering increases but strength decreases (Publication III).

3.4.4 Print rub fastness

Influence of PCC morphology

Samples printed on a HP LaserJet and Epson ink-jet printers had an average density of 1.5 and an average gloss of 3 and 2, respectively. These uncalendered and unsized handsheets are not suitable as such for print analysis. However, the relative changes in absorption (ink jet) and toner adhesion (laser printing) are relevant for understanding the role of the different filler types.

In the PATRA printproofness device, print was rubbed against an unprinted paper. The smearing caused by transferred ink in the unprinted paper was measured with a spectrophotometer according to ISO 11475.

The whiteness of the rub-off samples is illustrated in Fig. 18 which shows whiteness of a contact sheet, i.e., decreasing whiteness indicates high intensity of rub-off from the printed samples onto the contact sheet.

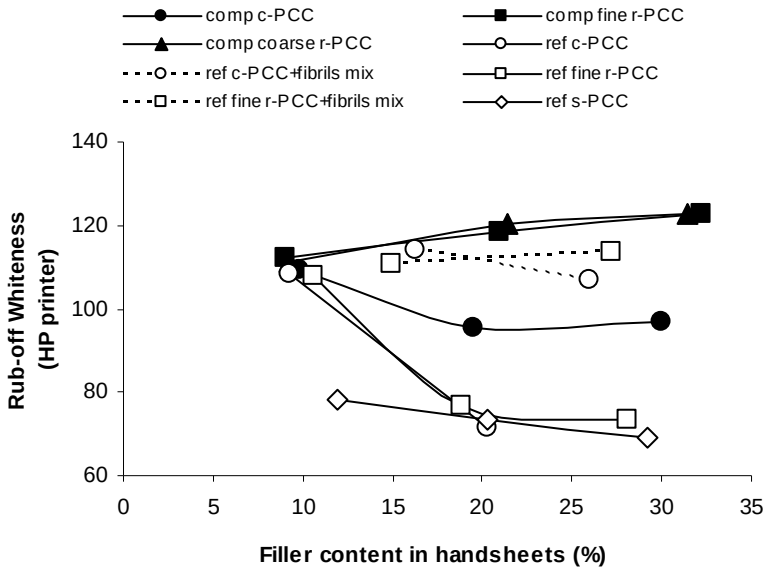

Figure 18 Rub fastness, measured as the whiteness of copy paper rubbing surface, of laser-jet printed handsheets formed with the addition of composite filler, conventional PCC's, with three different particle morphologies, and a PCC-fines mixture. Abbreviation: comp = composite; ref = reference, mix = mixture.

Addition of microfines, in the form of a composite or in a mixture of reference PCC and microfines, enhances the rub resistance of the printed samples. This effect is more pronounced at higher filler contents.

Addition of fines increases the sheet density of handsheets filled with composite and reference PCC-fibril mixtures. On the other hand, as shown in Figs. 7, 8 and 9, precipitation onto cellulosic pulp fibrils or mixing of microfines creates network structures consisting of a higher number of fine pores in contrast to the larger pore size of conventional reference paper. Lowering of the pore size, and thereby increasing the capillarity and adsorbing surface area, has a positive effect on print rub resistance /Gane, et al. 2006/. Gane's work deals with pores having diameter in the range of 0.1 µm to 10 µm.

Similar trends are observed with inkjet printed samples. With inkjet printing, due to the lower strength of the base paper, the surface of the reference sample was completely scuffed below 100 revolutions.

3.5 Conclusions

From the above discussion, and based on the study and suggestions by Xu and Pelton /Xu and Pelton 2005_a/, the following conclusions can be drawn for filled papers:

- The weakening of the mechanical properties of paper by filler is largely compensated by the addition of cellulosic microfines.

- Microfines are effective strengthening agents because they are able to bridge the filler-induced void in the fibre-fibre binding domain, acting as a glue strengthening the fibre-PCC and PCC-PCC contacts.

Thus, it can be deduced that acceptable strength for a fine paper can be obtained from celluloisic microfines alone. Hence, the fines-filler matrix is envisioned as a base furnish when aiming to significantly increase the amount of filler in paper.

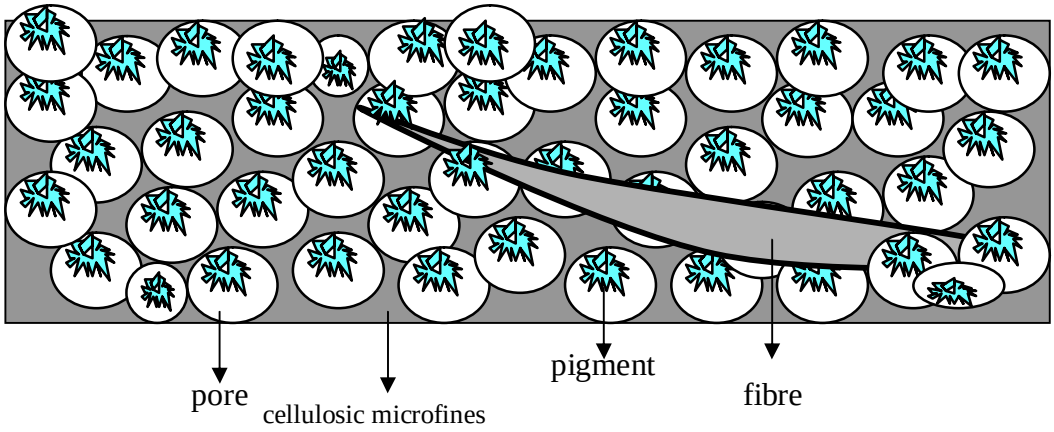

Figure 19 Network structure of new composite paper-type material.

On this basis, a new composite paper structure is postulated, as depicted in Fig. 19. Since fibrils provide much higher strength per unit mass than fibres, the matrix structure consists of filler surrounded by microfines. Fibres are interspersed in the matrix to reinforce the tear strength of the composite material.

The hypothesis concerning the new structure of a composite printing and writing paper was tested in the continued research.

CHAPTER 4

4.1 Fine paper produced from a new combination of raw materials enabling new combinations of technical properties

The aim of further experiments to be described was to produce uncoated wood-free paper containing a high amount of minerals, 50% or more, from a stock suspension of fillers, microfines, or chemical pulp fines, and fibres. In addition, this study aims to demonstrate the changes in structure-property relationships when we shift from fibres to pigment and microfines as the major papermaking furnish components.

Initial trials showed that it is possible to produce paper with a high fraction of minerals from a suspension of microfines and minerals. As expected, the tear strength of these samples was minimal due to the absence of long fibres. The aim was to improve the tear strength by adding 10-20% of unrefined eucalyptus kraft pulp, refined and fractionated bleached softwood kraft pulp and regenerated cellulose fibres. The experiments are described in Publication VI.

4.2 Procedure

4.2.1 Materials

A suspension containing cellulosic microfines was produced from non-dried elemental chlorine-free (ECF-) bleached softwood pulp consisting of a mixture of pine and spruce in equal amounts, using the Masuko supermass colloider®. The Masuko supermass colloider® is a special type of grinder which enhances the external fibrillation of the fibres /Kang and Paulapuro 2006/. In this device, the refining takes place between rotating and stationary stones with grits made of silicon carbide. The refining degree is increased by re-circulating the pulp suspension.

Earlier investigators /Silenius 2002, Retulainen et al. 1993, Retulainen et al. 2002, Seth 2003, Lin et al. 2007/ had used secondary fine particles that can pass through a 75 µm hole or 200 mesh of a fibre length classifier. On the other hand, we used more finely grinded homogeneous microfines in our study. 80 % of the microfines used in this work consisted of particles that pass through a 37µm hole or 400 mesh pass in a fibre length classifier. The characteristics of the microfines produced by the grinder have been described in another publication in which they are referred to as softwood bleached kraft (swbk) fines /Subramanian et al. 2008/. Each particle of the microfines, produced using supermass colloider®, comprises a developed intertwined network, as shown in Fig. 20. We found that these microfines are flexible and consist of micro and nano scaled cellulosic fibrils. They are capable of holding water as well as filler in the inter-fibrillar space of their network structure. However, we are yet to probe the differences in morphological and structural characteristics of the various types of

secondary fines, sourced from chemical pulps, and their performance in microfines-pigment composite handsheets.

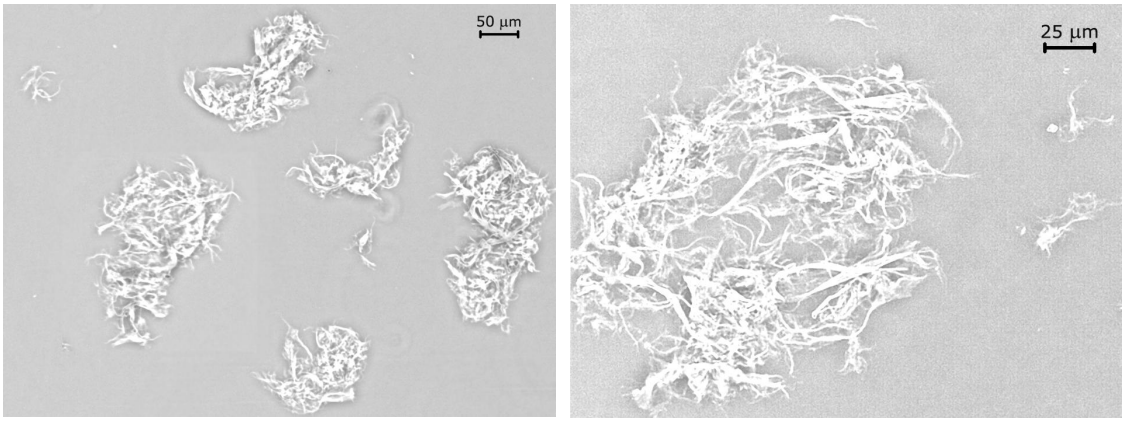

Figure 20 Negative phase contrast images of microfines obtained from bleached softwood kraft pulp; lower (left) and higher (right) magnification (after /Subramanian et al. 2008/).

Dried softwood, made from 60 % pine and 40 % spruce, was refined to 23ºSR and fractionated using a 30-mesh screen to obtain fractionated softwood fibres, used as long fibres in this study. Unrefined regenerated cellulose[4] and unrefined eucalyptus fibres were also used as reinforcement fibres.

Conventional laboratory reference handsheets were formed from the abovementioned non-fractionated softwood fibres and dried birch hardwood pulp refined to 28ºSR. A 70:30 mixture of hardwood and softwood pulp was used as the base furnish.

250g/t of C-PAM[5] was used as retention aid in the forming of the reference handsheets. Scalenohedral PCC with a mean particle size of 2.4µm was used as the filler pigment in paper.

4.2.2 Methods

After initial studies, an experimental plan was designed to produce new composite handsheets containing a minimum of 50 % PCC, with a grammage of 80g/m^2, as shown in Table. VIII. Initially, our plan was to use eucalyptus as the fibre fraction in the new composite materials. Subsequently, we formulated new recipes containing softwood and regenerated cellulose fibres to enhance the tear strength of the new composite materials. In addition, new 60 g/m^2 and 40 g/m^2 composite handsheets, reinforced with softwood, were produced.

The total volume of the stock suspension, in the new composite handsheets, was 500 ml with a consistency of 0.43 %. Handsheets were formed in a standard handsheet mould with a nylon fabric[6] on top of the mesh in the sheet mould. No extra water was added during forming. Nor were any additives added during the forming. The dewatering time of the handsheets was 3-4 minutes. Pressing and drying were carried out according to standard methods.

[4] Commercial regenerated cellulose fibres with the brand name Tencel were used in the experiments.
[5] Commercial C-PAM sold under the brand name of Fennopol was used in the experiment.
[6] Product name: SEFAR NITEX 03-10/2; mesh opening: 10µm

The reference handsheets were formed by standard method, ISO 5269-1:2005, in handsheet mould with the addition of retention aid. Handsheets containing long fibre and 30% microfines were formed at higher consistency (0.43 %), to lower the drainage time during the forming process.

4.2.3 Handsheet testing

Handsheets were tested in compliance with standard methods (Appendix). Two different test methods were used to estimate the fracture toughness of paper: fracture toughness and in-plane tear /Kettunen 2000/.

4.3 Results and discussion

The forming of the new composite handsheets was carried out with modifications in the standard handsheet mould. Dewatering time was, as to be expected, observed to be considerably longer. However, we are probing further to overcome this hurdle and we find, that retention aids addition or hydrophobic modification of fibrils can reduce significantly the dewatering time during forming. The impact of these modifications on paper properties will have to be investigated.

Table VIII Basic properties of new composite and reference handsheets.

Sample description				Sheet grammage (g/m^2) Average	PCC content (%) Average	Thickness (µm)	
No.	Microfines (%)	Fibres				Ave.	Conf. interval
		Eucalyptus (%)	Other (%)				
1	15	30	151	85.1	53.4	151	0.03
2	30	15	142	84.7	53.9	142	0.03
3	*30*	*10*	*140*	*84.9*	*49.7*	*140*	*0.1*
4	*30*	*10*	*109*	*63.3*	*51.7*	*109*	*0.03*
5	*30*	*10*	*74*	*41.3*	*51.3*	*74*	*0.04*
6	30	5	153	84.8	52.8	153	0.09
7	30	0	139	82.1	60.6	139	0.02
8	reference - conventional (lab) – Furnish: 70:30 hardwood:softwood			85.9	138	138	0.2

Note: Abbreviations: sw-softwood, RC– regenerated cellulose, conf. interval – 95% confidence level, No. – Numbering of test points.

The grammage, PCC content and thickness of the sheets formed are shown in Table VIII. The thickness of the handsheets formed in the laboratory, at the same basis weight, was the same both for the new composites and the reference samples. On the other hand, decreasing grammage significantly reduces the thickness of the new composite handsheets. Regenerated cellulose reinforced composite paper showed statistically higher confidence value compared with other samples.

The bulk and bending stiffness of the samples at various PCC contents are compared in Table IX. The bulk of the new composite samples is similar to that of a handsheet formed from conventional reference. It is known that the kraft microfines increases the density of fibre-based handsheets /Retulainen et al. 2002, Lin et al. 2007/. On the other hand, in an uncoated wood free paper made from microfines-filler-based furnish, PCC contributes to maintaining the bulk by restraining the collapse of the microfines during the drying process.

Table IX Bulk and bending stiffness properties of new composite and reference handsheets.

Sample description				Sheet grammage (g/m^2)	PCC content (%)	Bulk (m^3/t)		Bending stiffness (m Nm)	
No.	Microfines (%)	Fibres				Ave.	Conf. interval	Ave.	conf. interval
		Eucalyptus (%)	Other (%)						
1	15	30	0	85.1	53.4	1.77	0.03	0.19	0.12
2	30	15	0	84.7	53.9	1.68	0.03	0.28	0.05
3	*30*	*10*	10 (sw)	*84.9*	*49.7*	*1.80*	*0.1*	*0.33*	*0.01*
4	*30*	*10*	10 (sw)	*63.3*	*51.7*	*1.71*	*0.03*	*0.15*	*0.02*
5	*30*	*10*	10 (sw)	*41.3*	*51.3*	*1.79*	*0.04*	*0.04*	*0.02*
6	30	5	10 (RC)	84.8	52.8	1.71	0.09	0.21	0.04
7	30	0	10 (sw)	82.1	60.6	1.70	0.02	0.35	0.11
8	reference - conventional (lab) – Furnish: 70:30 hardwood:softwood			85.9	50.8	1.71	0.2	0.11	0.01

Note: Abbreviations: sw-softwood, RC– regenerated cellulose, conf. interval – 95% confidence level, No. – Numbering of test points.

At the same grammage, bending stiffness of the new composite samples are higher than the reference handsheets due to higher elastic modulus of the microfines-filler network. Comparing test points 1 and 2, we find that reduction of microfines proportion from 30 % to 15 % in the new composite paper contributes to lowering its bending stiffness. Among the three fibre reinforced composite handsheets, comparing test points 2, 3 and 6, softwood and regenerated cellulosic fibre reinforcement impart the highest and lowest bending stiffness property.

The microfines-filler-based handsheets contain high amounts of filler binded by microfines. Thus, we can postulate that the roughness will be lower compared to fibre-based fine paper. Highly smooth paper can be obtained by calendering of the new composite paper.

From test points 3,4 and 5 (Table IX), we observe that bending stiffness of the new composite paper significantly deteriorates when the handsheet grammage decreases from 80 g/m^2 to 40 g/m^2. Bending stiffness significantly at lower grammages due to decreasing thickness of the new composite paper.

Table X Permeability of the new composite and reference handsheets.

Sample description				Sheet grammage (g/m^2)	PCC content (%)	Permeability (µm/Pa s)	
No.	Microfines (%)	Fibres				Ave.	conf. interval
		Eucalyptus (%)	Others (%)				
1	15	30	0	85.1	53.4	1.3	0.06
2	30	15	0	84.7	53.9	0.2	0.02
3	*30*	*10*	10 (sw)	*84.9*	*49.7*	*0.3*	*0.02*
4	*30*	*10*	10 (sw)	*63.3*	*51.7*	*0.3*	*0.03*
5	*30*	*10*	10 (sw)	*41.3*	*51.3*	*0.5*	*0.02*
6	30	5	10 (RC)	84.8	52.8	0.6	0.2
7	30	0	10 (sw)	82.1	60.6	0.2	0.03
8	reference - conventional (lab) – Furnish: 70:30 hardwood:softwood			85.9	50.8	25	0.94

Note: Abbreviations: sw-softwood, RC– regenerated cellulose, conf. interval – 95% confidence level, No. – Numbering of test points.

The permeability of the handsheets as a function of filler content is shown in Table X. Reference handsheets, composed of an open network structure of fibres and filler, show the highest permeability. The permeability of microfines-pigments network, at various sheet grammages, shows very low air permeability. This is due to the

tortuous path and closed pores in the network structure, suggesting that microfines are also intimately bonded with the matrix blocking connectivity of the pore structure. Lowering of microfines amount contributes to enhancing the permeability of the new composite paper. On the other hand, comparing test points 3 and 5, we find that increasing filler content does not increase the permeability of the new composite paper.

Tensile and internal bond strength of the new composite and reference sheets are shown in Table XI. The new composite samples, at a grammage range of 80g/m^2 to 40g/m^2, exhibit significantly higher tensile and z-directional bond strength than fine paper made from fibre based reference samples. Among the new composite samples, reduction of microfines content, reinforcement with regenerated cellulose fibres deteriorate the bonding strength of fine paper. Comparing test points 3 and 7 which have similar base furnish composition, we find that increasing filler content above 50% decreases the strength of new composite handsheets.

Table XI Tensile and internal bond strength of new composite and reference samples.

Sample description				Sheet grammage (g/m^2)	PCC content (%)	Tensile index (kNm/kg)		Internal bond strength (J/m^2)	
No.	Microfies (%)	Fibres				Ave.	conf. interval	Ave.	conf. interval
		Eucalyptus (%)	Others (%)						
1	15	30	0	85.1	53.4	16.3	0.49	364	18
2	30	15	0	84.7	53.9	28.3	1.1	789	36
3	*30*	*10*	10 (sw)	*84.9*	*49.7*	*29.0*	*2.8*	*873*	*55*
4	*30*	*10*	10 (sw)	*63.3*	*51.7*	*32.2*	*1.7*	*646*	*33*
5	*30*	*10*	10 (sw)	*41.3*	*51.3*	*27.1*	*1.1*	*449*	*14*
6	30	5	10 (RC)	84.8	52.8	21.4	1.1	559	44
7	30	0	10 (sw)	82.1	60.6	27.0	3.0	470	32
8	reference - conventional (lab) – Furnish: 70:30 hardwood:softwood			85.9	50.8	7.80	0.3	220	12.9

Note: Abbreviations: sw-softwood, RC– regenerated cellulose, conf. interval – 95% confidence level, No. – Numbering of test points.

The new composite handsheets show significantly higher tensile strength compared to fibre-based reference paper. This is due to enhanced modulus of microfines particle network, inter microfines bond strength and relative bonded area. Reinforcing with regenerated cellulose fibres reduces the tensile strength of the new composite handsheets, due to the lower modulus and conformability of these fibres. On the other hand, softwood long fibres reinforcement enhances tensile strength due to improved bonding and activation of the network /Hiltunen 2003, Vainio 2007/.

Table XII Fracture toughness and in-plane tear strength of new composite and reference samples.

Sample description				Sheet grammage (g/m^2)	PCC content (%)	Fracture toughness (mJm/g)		In-plane tear index (Jm/kg)	
No.	Microfies (%)	Fibres				Ave.	conf. interval	Ave.	conf. interval
		Eucalyptus (%)	Others (%)						
1	15	30	0	85.1	53.4	1.90	0.2	2.45	0.4
2	30	15	0	84.7	53.9	2.05	0.1	3.24	0.3
3	*30*	*10*	10 (sw)	*84.9*	*49.7*	*5.98*	*0.8*	*6.85*	*1.1*
4	*30*	*10*	10 (sw)	*63.3*	*51.7*	*4.39*	*0.5*	*6.69*	*0.6*
5	*30*	*10*	10 (sw)	*41.3*	*51.3*	*4.02*	*0.9*	*6.19*	*0.4*
6	30	5	10 (RC)	84.8	52.8	4.89	0.9	5.04	0.7
7	30	0	10 (sw)	82.1	60.6	4.2	0.6	5.60	0.2
8	reference - conventional (lab) – Furnish: 70:30 hardwood:softwood			85.9	50.8	7.80	0.3	1.26	0.1

Note: Abbreviations: sw-softwood, RC– regenerated cellulose, conf. interval – 95% confidence level, No. – Numbering of test points.

The in-plane tear and fracture toughness is higher for new composite samples compared to conventional fibre based reference paper, Table XII. We find that the ability to avoid fracture at flaw significantly decreases when the amount of fines is lowered in the new composite handsheets from 30 % to 15 %. At a grammage of 80g/m^2, the reinforcing ability of the fibres in the new composite handsheets is in the following order: softwood>regenerated cellulose>eucalyptus fibres.

The fracture toughness of a composite material is a function of fibre length, bond density, fibre strength and bonding strength /Kärenlampi 1996, Seth and Page 1988, Hiltunen 2003/. In a microfines-filler network higher modulus of microfine particle network and enhanced bonded area and inter-microfines bond strength contribute towards its higher fracture toughness in contrast to fibre-based network. However, fracture resistance of the new composite handsheets depends significantly on the characterestics of the fibres used in the furnish and the amount of microfines fraction in the network. Bonding and conformable long fibres, like softwood, as well as higher microfines proportion contribute towards improving the flaw rupture-resisting ability of the new composite material.

Table XIII Light scattering and ISO brightness of the new composite and reference handsheets.

Sample description				Sheet grammage (g/m^2)	PCC content (%)	ISO Brightness (%)		Light scattering (m^2/kg)
No.	Microfines (%)	Fibres				Ave.	conf. interval	
		Eucalyptus (%)	Others (%)					
1	15	30	0	85.1	53.4	92.3	0.09	145
2	30	15	0	84.7	53.9	91.6	0.11	171
3	*30*	*10*	10 (sw)	*84.9*	*49.7*	*90.8*	*0.03*	*162*
4	*30*	*10*	10 (sw)	*63.3*	*51.7*	*91.1*	*0.05*	*162*
5	*30*	*10*	10 (sw)	*41.3*	*51.3*	*90.8*	*0.01*	*157*
6	30	5	10 (RC)	84.8	52.8	91.7	0.04	164
7	30	0	10 (sw)	82.1	60.6	92.5	0.06	175
8	reference - conventional (lab) Furnish: 70:30 hardwood:softwood			85.9	50.8	88.3	1.1	108

Note: Abbreviations: sw-softwood, RC– regenerated cellulose, conf. interval – 95% confidence level, No. – Numbering of test points.

Table XIII demonstrates that, the light scattering and brightness which increases already at high filler content in a conventional fine paper, is even more higher with the new composite material. Further, we find that lowering of microfines content in the new composite handsheet, contributes negatively to the light scattering of paper (compare test points 1 and 2).

The increased light scattering of the new composite handsheets can be attributed to the higher amounts of small sized optically active pores in the densified network. It seems that during consolidation process, shrinking of fibril network is restrained, leading to the creation of large number of micropores, apparently of light-scattering size. This has been confirmed by scanning electron microscopic studies, as detailed below. Reducing the amount of microfines in the new composites handsheets deteriorates the light scattering of paper. Thus, we find that the fraction of microfines is crucial in augmenting the light scattering ability of the composite handsheets.

Table XIV illustrates a comparison of tensile and tear strength against light scattering of the new composite and reference samples. From the table the following can be concluded:

a. A microfines-PCC-based fine paper significantly enhances the strength and light scattering of paper compared to reference.
b. In the new composite handsheets, increased amounts of microfines in the fibre-PCC network contribute to enhancing the tensile, tear indices and light scattering of paper.
c. From test points 2 to 7 we find that, in the new pigment-based handsheets softwood long fibre reinforcement improves the tear and tensile strength properties at comparable light scattering values.

Table XIV Light scattering vs. tensile and in-plane tear indices for the new composite and reference samples.

Sample description				Tensile index (kNm/kg)	In-plane tear index (Jm/kg)	Light scattering (m^2/kg)
No.	Microfines (%)	Fibres				
		Eucalpyptus (%)	others (%)			
1	15	30	0	16.3	2.45	145
2	30	15	0	28.3	3.24	171
3	*30*	*10*	10 (sw)	*29.0*	*6.85*	*162*
4	*30*	*10*	10 (sw)	*32.2*	*6.69*	*162*
5	*30*	*10*	10 (sw)	*27.1*	*6.19*	*157*
6	30	5	10 (RC)	21.4	6.10	164
7	30	0	10 (sw)	27.0	5.60	175
8	reference – conventional (lab) – Furnish: 70:30 hardwood:softwood			7.80	2.07	108

Abbreviations: Refer Table XIII.

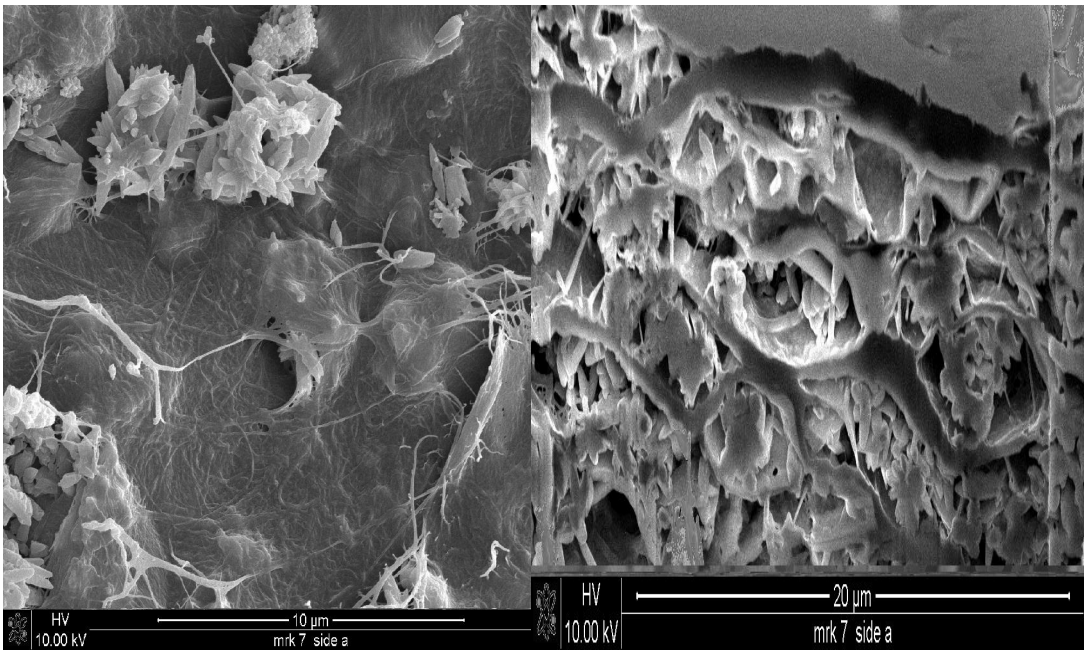

Figure 21 Z-directional SEM image of the new composite sample. The image on the left shows the entrapment of filler inside the microfines and the image on the right the network structure.

The structure of the composite material studied with a focused ion beam-scanning electron microscope (FIB-SEM). In FIB-SEM microscopy, the composite paper sample is coated with a thin Pt layer (to give sharp edges) and then the sample is cut completely distortionless with a focused Ga-ion beam in the Z-direction. The prepared sample is scanned and analysed using high-resolution imaging with an electronic beam. The Z-directional SEM image is shown in Fig. 21. As seen from the image, the microfines surround the PCC particles and form a network structure of PCC, fibrils and pores. Typically, pores have honeycomb-type of structure with

varying void volume. In addition, the surface SEM image (Fig. 22) show that fillers are firmly attached to the structure by cellulosic fibrillar films or fibrils of microfines.

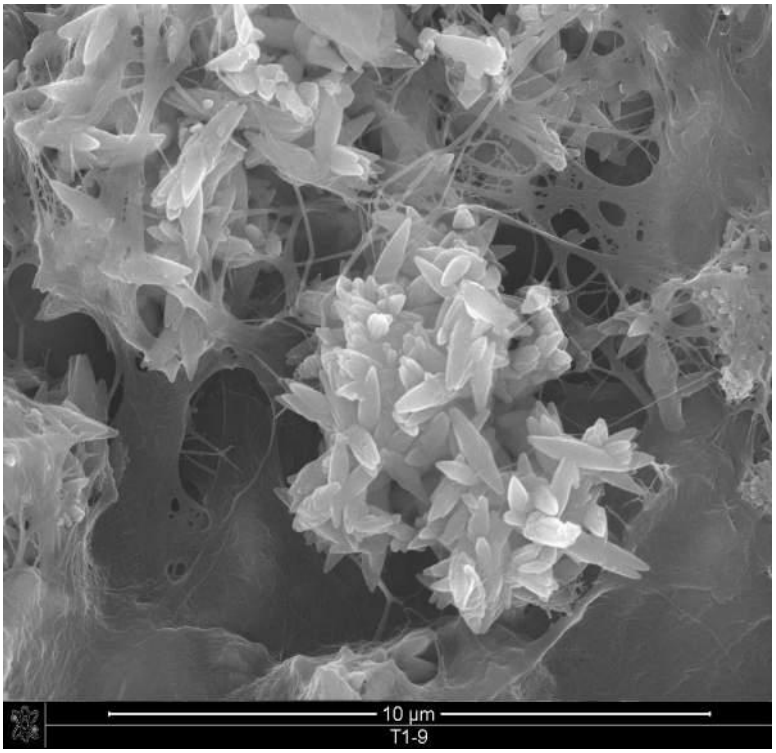

Figure 22 Surface SEM scanning image of the new composite sample.

4.4 Conclusion

This study describes the changes occuring in structure-property relationships in fine paper when the base furnish changes from fibres alone to fines-pigment mixture. The new composite paper concept enables us to load upto 50 % - 60 % PCC in fine paper. Compared at similar grammages and high filler loading, a network of fine paper formed from microfines-filler-based furnish exhibits similar bulk, and higher bending stiffness, bond strength and optical properties than conventional fibre-based reference samples. On the other hand permeability of the new composite paper decreases significantly, suggesting that microfines are also intimately bonded with the matrix blocking connectivity of the pore structure.

In the new composite handsheets, higher proportion of microfines and the reinforcing fibres with better bonding potential and conformability significantly improve the strength and tear of paper. Lowering of basis weight deteriorates the thickness and bending stiffness of the new composite handsheets.

We elucidate, based on FIB-SEM studies that in the new composite handsheets the microfines and filler form a continuous structure interspersed by fibres. Since the bond strength and relative bonded area of microfines is higher compared to fibre, the strength of the new composite copy paper network is considerably improved in comparison to a fibre-based fine paper. The microfines-pigment network is composed of a higher number of small sized optically active pores, and hence, the brightness and light scattering of these samples are better than fibre-based fine paper.

CHAPTER 5

Conclusions

This study explores avenues to exploit the intrinsic material values and functionalities of cellulosic pulp fibres and pigments at micro- and nanoscale as a means to engineer new and higher quality uncoated wood-free paper.

The first hypothesis was:

- Filling the wet sheet of paper allows higher retention of filler and a means to manipulate the bond properties of paper.

The goal of this preliminary study was to fill the paper by precipitating using ionic solutions or applying the pigment, calcium carbonate, onto fibre web and then, compress mechanically to assist the pigment to penetrate into the network. One of the aims was to obtain an even distribution of pigment in the z-direction of paper.

Initial trials showed that precipitation of calcium carbonate using calcium chloride and sodium carbonate solutions results in yellowing of handsheets. Hence, the pigment was crystallised using calcium chloride and ammonium carbonate solutions. Calcium carbonate was directly applied at higher concentrations using dispersed ground calcium carbonate solutions.

According to the results obtained in the study, we found that the precipitation calcium carbonate show the highest tensile index and lowest light scattering for paper compared to reference samples. We observed that the calcium carbonate was agglomerated during crystallisation in handsheets. Thus, the wet web precipitated calcium carbonates did not significantly disturb the fibre-to-fibre bonding in paper. Because of the minimal effect on strength properties preventing agglomeration by modifying the precipitation conditions could offer the possibility to use very high amounts of filler in fine paper.

Application of ground calcium calcium carbonate was carried out spraying the filler onto the wet web of paper and subsequently, mechanically pressing the handsheets. Initially, filler addition reduced the tensile index of paper. Increasing filler content in handsheets, greater than 20%, did not have any impact on the tensile strength of paper. In addition, wet web application did not improve the light scattering of paper. Accumulation of filler on the sheet surface resulted in optical crowding, and hence, the light scattering was distinctly lowered.

In this study, the experimental conditions were not sufficient to obtain even distribution of filler in the z-direction of paper and filler characteristics were not optimised. Further, filler agglomeration and optical crowding of calcium carbonate resulted in deteriorating the light scattering of handsheets formed by precipitation and spreading techniques.

The second hypothesis was:

- If paper is viewed as a continuous matrix of solid components, the surface area for bonding and the internal surface area associated with the pores can be manipulated by precipitating PCC in-situ onto the cellulosic pulp suspension. In-situ precipitation of calcium carbonate onto the fibre fibrils provides an approach to increase the filler in paper by minimising the effect of filler on sheet strength, while maximising the apparent light scattering of paper. The product performance of PCC precipitated on top of pulp fibrils can be enhanced and optimised by modifying the raw material components, methods of production and crystal habits of the precipitate.

To examine the above hypothesis, three different types of experimental approaches were tested. They are:

1. Effect of pulp substrate
2. Influence of PCC morphology
3. Refining pulp and milk of lime together, and then subsequent precipitation of calcium carbonate

In examining in-situ precipitation of calcium carbonate onto refined pulp fibrils, the following conclusions can be presented:

In the first study, PCC was precipitated onto five different fibrillated wood and non-wood pulp suspensions. Analysing the precipitated PCC composite fillers, we found that the filler attachment is high with non-dried softwood and hardwood fibrillated pulp suspensions. The z-directional bond strength of handsheets composed of baggase composite is significantly higher than the reference. Based on the pulp substrate used for in-situ PCC precipitation, the internal bond strength of composite filler containing handsheets decreases in the following order: bagasse, pine, birch, mixed hardwood (India) and rice straw. On the other hand, pine and rice straw composite filled handsheets exhibit the highest and lowest light scattering for the copy paper. Increased fibre fibrillation, augmenting the surface area available for bonding, in combination with suitable PCC morphology contribute to improved internal bond strength and light scattering of paper.

From the second investigation, we deduce that PCCs formed by precipitation of calcium carbonate onto cellulosic fibrils and fibres do not necessarily have the same characteristics as reference PCCs formed by carbonizing milk of lime. For example, presence of fines hinders and inhibits the growth of scalenohedral crystals, leading to holes in their structure and differing particle characteristics compared to the respective reference precipitates.

The laboratory studies show that the precipitation of calcium carbonate onto refined pulp fibrils increases the retention of fillers during forming. The mixture of reference filler and fines was found to result in a higher retention than only reference filler but lower than the composites. Mixing of filler and fines traps the filler into the fines network, resulting in higher retention than when using the reference filler by itself.

On the other hand, solid contents after pressing show that higher amounts of composite filler addition cause the dewatering of handsheets to deteriorate. The network formed by the different crystal habits of the precipitate determines the dewatering behaviour of the composite handsheets. Flocculation and expansion of the network structure has a positive impact on dewatering, while film-forming fines retard dewatering and result in higher moisture in pressed handsheets.

In fine paper, augmenting of cellulosic microfines results in higher density, bending stiffness, and lower sheet porosity. Increased amounts of cellulosic microfines, added either as a PCC co-crystallised onto fines or PCC-fines mixture, contributes to enhancing the bonding and activation, thereby improve the tensile and internal bond strength indices of fine paper. Among the different crystal habits studied, r- and s-type PCCs, with higher average particle size and lower specific surface area, debond to a lesser degree. Hence, they enhance the inter-fibre bonds in the network, and thus, improve the strength of paper.

Even with increased density, composite fillers containing handsheet show comparable or better light scattering than fine paper formed by traditional methods. The increase in light scattering might attributed to the formation of filler-fine complexes which lead to higher number of small sized optically active pores in the densified network.

Addition of fibrillar microfines, in the form of a composite or in a mixture of reference PCC and microfines, enhances the rub resistance of the printed fine paper samples. Precipitation onto cellulosic pulp fibrils or mixing of microfines creates network structures consisting of a higher number of fine pores with augmented capillarity and adsorbing surface area. This has a positive effect on print rub resistance.

Based on the third method, we explain that refining pulp and calcium hydroxide together leads to grinding of lime, and hence, the composite PCC has a greater surface area than the reference filler. Even at a low refining degree the in-situ precipitated PCC formed by this process imparts higher light scattering to paper. On the other hand, the composite filled handsheets exhibited debonding characterestics similar to that of the reference samples.

Based on the research related to the second hypothesis, hypothesis 3 was formulated. According to this hypothesis:

- Microfines-filler is envisioned as the backbone structure of a new composite paper-type material in which the strength properties arise from the microfines, bulk and pores emerge from the filler surrounded by the cellulosic fibrils, while the tear strength comes from the minimal fibre fraction in the composite.

After initial studies, the we formulated and produced new composite handsheets with the following compositions:

1. Precipitated calcium carbonate (PCC) for bulk, optical properties, porosity and shrinkage reduction; proportion in the furnish – being set to 60 % or lower
2. Cellulosic microfines for tensile strength and bending resistance; proportion in the furnish – being set to 30 % and 15 %
3. Fibres for tear; proportion in the furnish – being set to 10 % - 30 %

The results show that the thickness of the new composite and reference samples were similar. The bulk of fines-filler based copy paper handsheets were similar to that of conventional reference laboratory handsheets.

Bending stiffness of the new composite handsheets is higher than the reference handsheets due to higher elastic modulus of the microfines-filler network. Decreasing grammage reduces the bending stiffness of the new composite handsheets significantly, due to diminishing thickness of paper.

The fibre-based handsheets show high air permeability. In contrast, permeability of microfines-pigment network show very low air permeability. increasing amounts of PCC in a fibre-based handsheet results in enhancing the air permeability of handsheets. This is due to the to tortuous path and closed pores in the network structure, suggesting that microfines are also intimately bonded with the matrix blocking connectivity of the pore structure.

Tensile and internal bond strength of the new composite handsheets are higher than fibre-based conventional reference paper. This is due to enhanced modulus of microfine particle network, inter microfines bond strength and relative bonded area. Among the new composite samples, reduction of microfines content, reinforcement with regenerated cellulose fibres deteriorate the bonding strength of fine paper. On the other hand, softwood long fibres reinforcement enhances tensile strength due to improved bonding and activation of the microfines-pigment network.

The in-plane tear and fracture toughness is higher for new composite samples compared to reference. The reinforcing ability of the fibres in the new composite handsheets follow the following decreasing order: softwood, regenerated cellulose and eucalyptus fibres. In a microfines-filler network higher modulus of microfine particle network and enhanced bonded area and inter-microfine bond strength contribute towards its higher fracture toughness in contrast to fibre-based network. Bonding and conformable reinforcement long fibres, like softwood, as well as higher microfines proportion contribute towards improving the flaw rupture -resisting ability of the new composite material.

The light scattering and brightness which increases already at high filler content in a conventional fine paper, is even higher with the new composite material. In the new composite handsheets, it appears that the fibrils shrinkage is prevented during the consolidation process leading to the creation of optically active pores. The presence of high amounts of filler and optically active pores significantly enhances the brightness and light scattering of fines-based composite handsheets.

We conclude that the new concept of fines-pigment-based furnish enables us to load pigments in uncoated wood free paper upto 50 % - 60 %. We confirm, based on FIB-SEM studies that in the new composite handsheets the microfines and filler form a contiguous honeycomb-like structure interspersed by fibres. However, microfines are highly swollen and difficult to dewater. Thus, as expected, dewatering time was observed to be considerably longer. Further studies on dewatering, high-consistency forming, printing and optimisation are required to scale up this technology into an industrial process.

To summarize, this study enunciates the possible different approaches to form a novel uncoated wood free paper. We enunciate that it is possible to increase the fraction of filler in fine paper significantly by utilising the structural elements of the raw materials. Further studies are required in process optimisation, and as usual, when applying a papermaking technology the final optimisation has to carried out in a mill scale process.

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APPENDIX

Relevant test methods used in the experiments and their standards

Test Methods	Test Standards
Grammage	ISO 536
Determination of thickness and bulk density or apparent sheet density	ISO 534:1998
Determination of air permeance	ISO 5636-3:1992
Determination of tensile strength – Part 2: Constant elongation method	ISO 1924-2:1994
Internal bond strength	T 569 pm-00
Fracture toughness and In plane tear strength	Scan-P 77:95
Bending stiffness	ISO 2493:1992
Opacity	ISO 2471:1998
Brightness	ISO 2470:1999
Light Scattering	ISO 9416-1998
Ash content	ISO 2144:1997